Journal
of
The Franklin Institute
Devoted to Science and the Mechanic Arts

Vol. 203 MAY, 1927 No. 5

THERMIT AND ICEBERGS.*

BY

HOWARD T. BARNES, D.Sc., F.R.S.

Professor of Physics, and Former Director of Physics, McGill University, Montreal.

THE temperature balance between ice and water is most delicate. When the equilibrium is upset a minute fraction of a degree, sometimes too small to be recorded on a sensitive thermometer, one phase will pass over to the other. A temperature gradient must be produced across the boundary surface between solid and liquid for the heat to flow, and the change to proceed.

Researches done by the writer thirty years ago showed this to be true, and these results have thrown much light on the behavior of ice in nature.

The true freezing-point of water has to be defined as an intimate mixture of ice and water neither gaining, nor losing heat. In large ice accumulations of lakes and rivers, the only difference between ice masses tightly bound and the same loose and soft is no more than a thousandth of a degree. Large temperature changes in the system *ice-water* or *water-ice* are impossible, for the velocity of transformation is rapid enough to prevent supercooling or heating to any great extent.

Practical applications of heat to compensate this small temperature effect have been made to prevent ice accumulations. Ice prevention requires vastly less actual heat than getting rid of ice after it has formed. This is a fact, however, which few engineers appear to realize.

Heat has been applied in the form of steam or electrical energy

* Presented at a meeting of the Institute held Thursday, November 11, 1926.

(Note.—The Franklin Institute is not responsible for the statements and opinions advanced by contributors to the JOURNAL.)

COPYRIGHT, 1927, by THE FRANKLIN INSTITUTE.

with varied success, but with the great development of hydro-electric power of recent years, involving such large turbines and volume of flow, more powerful methods of ice control have become necessary. The use of dynamite and other explosives for ice fighting is limited to open areas away from settled communities, and fixed structures, and is resorted to not as a preventive measure, but as a last resort in emergency.

It is reasonable to look to heat as the natural fighting tool, and nature points the way in directing us to the powerful influence of the sun. Great power houses, shut down during a cold night, are at once relieved in the morning with the sunrise. The penetrating power of the sun's rays unbinds the forces of freezing between the ice crystals, honeycombs solid ice, without necessarily melting them. The actual energy radiated into water by the sun is not so great as can be supplied locally by steam, but the character of the radiation from a high-temperature source is such as to give it great penetration, and widespread influence. Water is almost opaque to rays which come from a radiant below a low red heat, but the energy from a high-temperature source has great penetrating power. When steam or electric heaters are put in water the action is confined to the surface in mechanical contact, and the spread of the heat is only brought about by stream lines of flow.

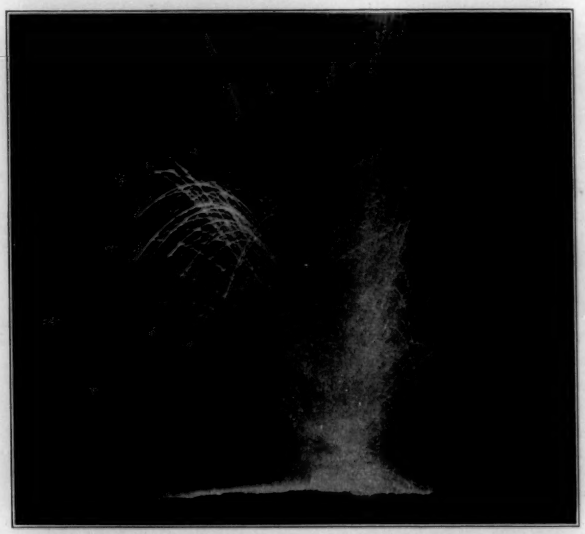
In selecting a radiant beam for ice control, the selective absorption of water for heat rays has to be carefully considered. In solid ice the problem seems to be a similar one, and the whole matter appeared to the writer in a new light in 1924, when making iceberg studies off Newfoundland, as will be explained later in this paper. The actual solution of the problem came only after considerable experimentation during the winter of 1924–1925 in the ice packs of the St. Lawrence River. A material had to be selected which could be readily applied under difficult conditions in the open under the ice in a river, be moderately economical to use and safe to handle, and which would give as complete an imitation of the sun's rays as possible. As the sunlight is scattered by the surface ice of a lake, or river, the energy, so valuable for ice prevention, is entirely lost and cannot be recovered. Could we direct the sunlight under the ice where the water is comparatively warm as contrasted with the air above, then little or no ice could form, and that which did on a cold night would be rapidly dispersed on a clear day.

An exothermic mixture of aluminum metal and iron oxide is easily obtained which answers well the conditions sought and can be easily applied in suitable containers anywhere. The material known to the trade for twenty-five years as *thermit* fulfills this requirement very well.

THERMIT HEAT UNITS FOR ICE CONTROL.

The heat from reacted thermit is so intense that the mass of molton iron which carries the heat is too bright to look at

FIG. 1.



Solid block of H_2O ice burning and flying to pieces under the fierce heat of a thermit charge.

without dark glasses. A temperature which varies from 2500° to 3500° C. is produced in a few seconds. The actual number of heat units per pound of material is only 1500 and is much less than for coal, but the temperature being so high this small amount of heat is very effective for the purpose of ice control. Then the energy back of the reaction, while not great compared to carbon, is sufficiently large to give a powerful energy flow for a

considerable time. Such energy when delivered from a body at so high a temperature is far more effective than many times more actual heat units at a lower temperature, such as steam or burning coal would impart.

As soon as the molton iron comes in direct contact with the ice or water a second reaction takes place which decomposes the H_2O into oxygen and hydrogen. The oxygen is fixed by the iron to form the oxide again, and the hydrogen is liberated and burns with the oxygen of the air. There is such a rapid evolution of gas that a slow explosion results, which has proved most effective in loosening and cracking ice masses. It is well known how steam is dissociated into O and H when passed over red-hot iron and this gives a convenient way of preparing hydrogen gas. The thermit does the same thing with ice or water on account of its very high temperature, and imparts two very important properties for ice fighting, *i.e., heat* and *explosion*. The reaction makes little or no noise and is admitted by experts to be the slowest explosion known. On account of this fact it can do no harm to concrete structures, or bridge piers in immediate contact with the reacting thermit, and no harm has ever been done to fish in rivers or lakes where it has been used.[1]

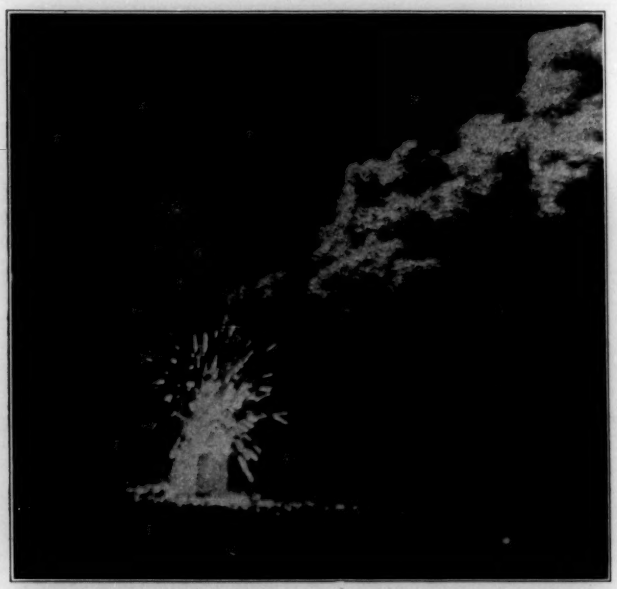
For ice control in thickly settled communities it offers no unpleasant or dangerous features for there are no detonating noises to break windows, and the thermit is itself absolutely non-explosive and safe to handle and transport. The writer does not attach importance to the amount of ice which thermit actually

[1] To test the theory of the thermit ice reaction giving rise to the production of hydrogen gas Dr. D. A. Keys, of McGill University, kindly placed at my disposal a strong iron reaction bomb in which he had studied gas explosions. Accordingly the thermit reaction was put off in this enclosed space along with ice. After the reaction had been consummated, gas under pressure was liberated through a stop-cock which burnt with the hydrogen flame. This experiment is being repeated with Doctor Keys for the object of securing the hydrogen spectrum.

Another test was made of the thermit reaction in solid carbon dioxide ice. (Figs. 2 and 3.) A block of "dry ice" one foot square was prepared with a hole drilled to the centre and a charge of thermit placed directly in the hole. The reaction resulted in dense carbon smoke, but no explosion. A second trial was the same with a larger charge of thermit. A triple crack came as a result of this, but no explosion. A third attempt with yet more thermit caused the block to explode with no noise, and no sign of the hydrogen gas burning as is characteristic of the ice explosion. The explosion was probably due to some moisture in the carbon dioxide.

melts for the heat liberated is small compared to the heat of fusion of ice. The important fact is the output of energy in a penetrating heat ray which overcomes the exceedingly small temperature effects in the water responsible for the pranks and incon-

FIG. 2.



Solid block of CO_2 ice burning under thermit charge.

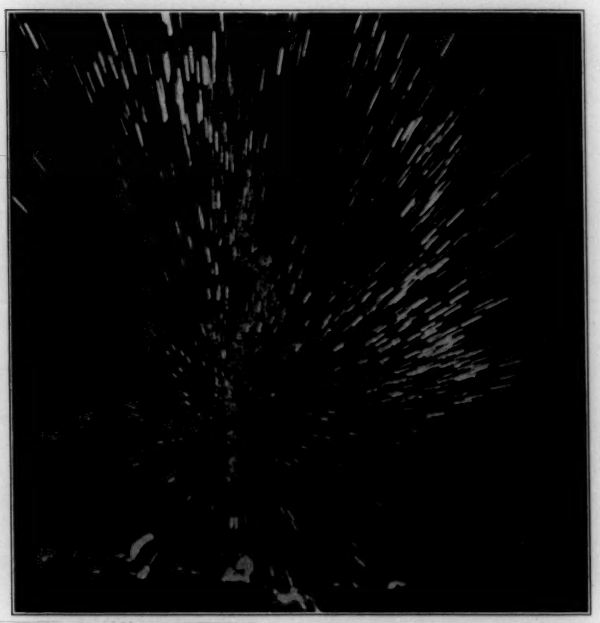
veniences caused by ice. It is possible to see thermit heat units glowing through several feet of water and ice masses, which proves the penetrating power of the radiation.

The reaction of thermit has been studied in solid ice and Fig. 1 shows a block of ice weighing 400 pounds, blown to pieces with a charge of two pounds of thermit reacted in a hole cut in the block about half way through, but not sealed. The picture shows the great volume of hydrogen gas driven out and upwards to a height of 70 feet with the heavier molten slag and iron falling in a

shower of fire all around. When this reaction is made in a closed bomb the hydrogen can be collected and burnt with ease.

The reacting charge, when first fired, glows with an intense white heat inside the ice for several seconds before the explosion

FIG. 3.



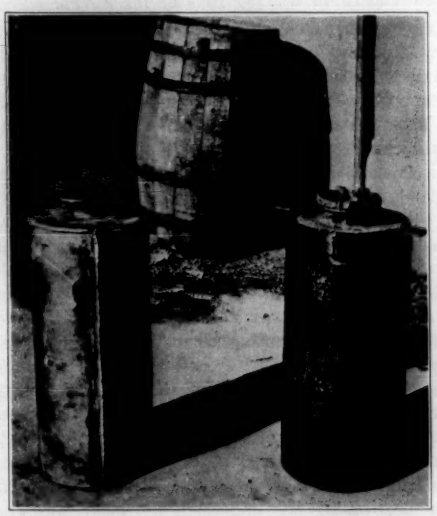
Solid block of CO_2 ice exploding under a second charge of thermit.

occurs, and proves how powerfully the rays are sent out through the ice for the whole block seems to be white hot. It may be that the ice becomes superheated just before the final explosion, because the slow motion picture of the reaction shows a vapor given off from the outside of the ice immediately preceding the upheaval. Undoubtedly temperature strains are set up in the ice, especially when it is very cold, and to these temperature strains is attributed the great cracking which goes on in an iceberg for

many hours after a thermit heat unit has been fired in it. An iceberg gives the best example of the effect of the strain, as it is by far the largest mass of solid hard ice that could be experimented with.

The result of bringing a body at such a high temperature in

FIG. 4.



Samples of the first two thermit heat units used. February, 1925.

contact with cold ice was quite unknown to the writer before these experiments were tried. In fact, the passage of heat across a very steep temperature gradient has never been studied, nor the mechanism of transfer determined. Ordinarily we would regard it as conduction, but what this method of heat transfer becomes when the gradient is several thousand degrees across a face of perhaps molecular dimensions is difficult to visualize.

The first experiments made on the St. Lawrence in February, 1925, were approached with great caution. The explosive action of the heat input in ice was not entirely anticipated, and the design

of a suitable container and the best method of applying the charge was largely a matter of trial.

The writer was fortunate in being able to consult Major H. B. Faber, Director of Military Pyrotechnics of the U. S. Army, who rendered invaluable help, and through his interest and coöperation greatly facilitated the experiments. (Fig. 4.)

QUARTER MILLION TONS OF ICE MOVED.

The first experiments were tried at Waddington, N. Y., on February 24, 1925, in a great ice jam in the south channel of the St. Lawrence River, Major Faber being present during the experiments. The location selected lay between the main shore of New York State and Clark Island, where a large jam of ice blocked the channel just below the Pulp Wood Dock. A large field of ice, which had formed on a shoal between Ogden and Clark Island, became detached with a temporary rise of water and lodged below the Pulp Wood Dock, completely closing the south channel. This occurred on or about the twentieth of January. Thereafter a considerable accumulation of the usual floating ice packed firmly along the head of the lodged ice sheet, creating a head of water of a foot or more. The process of accumulation continued, causing a pack which was further accentuated by shoves.

At the time of these experiments the jam was approximately 1000 feet in length and 500 feet in width. The accumulated mass under the ice sheet was carefully measured, showing depths varying from six inches to 43 feet. The head, foot and sides of the jam were lodged solidly on the bottom, so much so in fact that the upper portion of the underhanging mass was compacted appreciably. In choosing locations for the operation of the heat units two points were selected near the head of the jam in the centre of the channel and the third was located near the foot also in mid-channel, but in the centre of a solid mass of slush ice 38 feet thick, resting on the bottom.

The first container, holding about 90 pounds of thermit, was inserted through a hole about two feet square cut at the first location through the surface ice eight inches thick. On the under side of this sheet was found underhanging slush ice to the depth of 13 feet. The container was lowered into the hole, suspended by four steel ropes and with difficulty pushed through the underhang to a depth of eight feet; the wires were fastened to four

wooden stakes driven into the ice. The wires for igniting the thermit were 50 feet long and connected to a storage battery. This length was considered a safe one as no violent outward reaction was anticipated.

Doctor Faber took charge of the firing, and when it was estimated that the reaction was complete, the ice was observed to upheave and a great wave passed through the entire ice field and a column of water and shush mixed with hard ice, was hurled 20 feet into the air, mushrooming to a diameter of 40 feet.

After the reaction had subsided in the course of four or five minutes the container was removed with difficulty owing to the disintegrated character of the ice near the hole. It was found that the molten iron had gone right through the bottom directly into the ice mass. The hole in the ice had been blown to 25 feet in diameter through the solid ice, but slush ice from below had risen in a dense compact mass which enabled the men to support their weight in a reclining position to rescue the container for examination. Further examination revealed another crack 50 feet in diameter surrounding the original hole, and perfectly circular.

The time being late, the other experiments were put off until the following day. The writer expected that owing to the distribution of the heat generated it would take at least twenty-four hours to see outward visible effects under the ice at outlying parts of the jam. The head of water was expected to seep in through the openings made by the heat unit and gradually wash its way along, undermining the pack. That this surmise was correct was not only substantiated in this case but has been in all other cases of subsequent use of the units. The disruptive actions of the units find their greatest and most effective action in this effect.

Every unit put off in an ice pack acts as a point of infection which spreads over a greater and greater area until the water melts its way through and comes out through the hole blown in the ice, it then cuts its way down this pack whenever the pack remains long enough in position for it to go on acting so. In the Waddington jam, however, the other two containers put off brought out the entire mass of ice within twenty-four hours, but this cutting and undermining action of the flowing stream under the surface was noticeable. The second experiment was made by inserting a unit in the mass midway between the scene of the first unit and an opening in the middle of the jam cut out by the

heat of the first unit. Longer wires were put on, and two extra batteries were attached. The unit was put down three feet in slush under the surface ice. The reaction resulting from this firing was different from the previous one and there was noticed two primary and three secondary upheavals which shattered the surface ice and then a huge flame 15 feet in diameter and six feet high was emitted which burned for several seconds over the hole. This was interesting and startling, as it was the first demonstration of the decomposition of the ice into its gases with actual phenomenon of burning ice.

The last experiment was carried out within a few minutes of the second, and it was placed at the lower extremity of the jam down 20 feet in the huge mass of slush forming the foot and main support of the jam.

On firing no outward sign of the reaction was visible, but the whole pack was shaken by the upheaval like an earthquake with a dull, low, rumbling sound. As the time was late, the party returned across the river to their homes and the jam was left for the heat to act during the night. It is proper to mention that following the experiments the weather turned intensely cold, which was a condition favorable to holding the jam in place, strengthening the mass and adding to it by infiltration of freshly formed river ice. A close watch was kept all the next day to detect any visible sign of the heat action. Nothing of importance was noticed until the afternoon, when some floating masses of ice were seen moving away from the foot of the jam. After an interval of about half an hour the whole jam moved out of about 250,000 tons of ice, and passed quietly down the river, leaving the channel clear. As the ice moved away some heavy masses grounded about two miles down stream, where they remained firmly in place in a current of high velocity. The river at these points is of sufficient depth to pass the usual river ice without obstruction. An examination of these grounded masses showed evidence of the heat units, for the slag from the molten thermit was embedded therein.

It is well to point also that the jam was an old established one which was wedged in precisely in the form of a cork in a bottle. The sides were sustained by heavy natural field ice of unusual strength firmly locked in position and in the ordinary course of events no movement would have taken place until the spring

break-up. As proof of this there was no other movement of ice fields observed along the river and the jam at Chimney Island was reformed and strengthened concurrently with these experiments.

ONE MILLION TONS OF ICE MOVED.

The success with the experiments in the Waddington ice jam encouraged the writer to try some of the heat units on a larger jam. During February and early March a heavy pack had formed in the south channel between Chimney Island and the New York shore below Ogdensburg, which had gradually filled with snow and loose pack ice from the river above. The river level had been lowered below by about a foot and in consequence was backing the water up into Lake Ontario. There was no immediate prospect of this jam moving out, as it was securely wedged by very heavy barriers of pack ice grounded in some places in 70 feet of water. Some of this pack ice was shoved up from the bottom to a height of seven feet above the water level. A more difficult or unpromising field of operation could hardly be selected. On February 19th, the jam was visited and preliminary measurements made with photographs. On March 11th and 12th a rough survey was made and the key of the jam located. On March 13, 1925, two heat units of 90 pounds each were set off at two places considered the most vulnerable. The first shot was placed under the surface ice, which was 27 inches thick and exceedingly hard with no underhanging ice. The hot iron passed directly into the running water without much explosion, but directly after the water could be heard flowing violently along the channels cut under the ice by the heated material.

The second shot was placed about 200 feet south in an underhanging mass of slush. The surface ice was 20 inches thick here and the depth of the underhang was eight feet. The unit was forced down four feet and tied to four steel ropes attached to stakes as before. On firing, a heavy explosion ensued and a hole 15 feet in diameter was blown in the hard ice. A flare of intense heat and flame shot out to a height of 45 feet and 20 feet in diameter. (Fig. 5.) After this, flames played over the hole for five or six seconds. This shot cracked the ice for a distance of 600 feet and a three-inch surge of the water was observed in the opening 200 feet away, where the first unit had been fired.

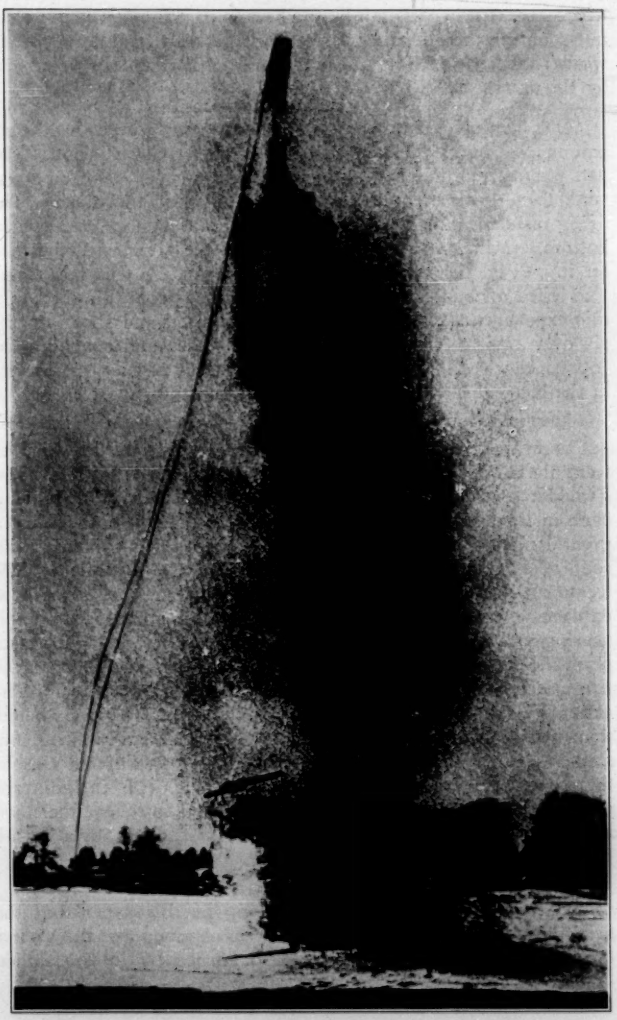
Having completed the firing of all the remaining units which the writer had to use in these experiments, the scene of operation like that at Waddington was left for the night for the effects of the shots to have full play. In exactly nine hours after, the key of this jam came away where it had been treated, and during

FIG. 5.

Reaction of 90 pounds of thermit in the Chimney Island ice jam. Reversal of image of flaring gases is shown.

the night the whole jam moved out as well as two larger ice fields which were loosened above probably by the change of water level which resulted. The fields being large areas of surface ice dislodged above. The channel was quite clear by the evening of the next day and in a week's time all the ice had moved down the river. With the removal of this jam the river levels below were restored to normal in a day or two. An estimate of the amount

FIG. 6.



Reaction of 90 pounds of thermit in an ice jam at Clark Island.
Note the container rifled up 100 feet in the air.

of ice liberated in this jam by the heat units was one million tons, not counting the other two floes which passed through and which would have packed into the ice jam had it not been taken out by the units.

ICE PAN REMOVED AT CLARK ISLAND.

One heat unit of 90 pounds of thermit was placed in a heavy pan of ice grounded in nine feet of water near Clark Island. The pan was approximately 8500 square feet in area. The unit was sunk to a depth of four feet in the underhanging slush. The firing resulted in an explosion which lifted the entire pan off the bottom, cracking it and floating it down the river with the man on it. (Fig. 6.) In addition another pan 60 feet away was also lifted off and floated down by the surge from this shot. In this experiment the heavy iron container rifled and shot into the air over 100 feet, pulling out the four stakes and snapping the four steel wires like threads. The operators rescued themselves in the boat which they had used to land on the pan.

REMOVAL OF THE ALLEGHENY ICE GORGE WITH HEAT UNITS.

In March, 1926, the writer was called out to Oil City to treat the huge ice gorge which was threatening Oil City and Franklin on the Allegheny River. This was a dry jam holding back in flood the waters of the river and placing both cities in great danger as well as the whole extent of the Pennsylvania Railroad track for 25 miles between Oil City and Brandon. The treatment of this mass of ice with its subsequent removal without damage forms an important chapter in the history of ice engineering written for the first time. It is too long a story to relate here and it has already been told in a paper read before the Engineering Institute of Canada. (November, 1926.) The action of the thermit heat units of large size was even better than had been anticipated and the gorge was literally burnt and shaken loose from the shores by the thermit treatment. About three tons of dynamite were also used but with insignificant results. Less than five tons of thermit served to relieve the flood and remove the ice from the lower end first, thus obviating all further chance of damage.

ICEBERG DESTUCTION.

It was pointed out at the beginning of this paper that the first idea of using thermit in ice was obtained by the writer during a study of the disintegration of an iceberg in 1924 when

the guest of the U. S. Coast Guard Ice Patrol off the coast of Newfoundland. The application of intense heat in an iceberg was delayed for a long time, but in the interim the experiments in the ice packs of the St. Lawrence as just described were carried out. The reasons for the anticipated disrupting action of intense heat will now be set forth as briefly as possible. While watching the iceberg break up in 1924 the writer repeatedly observed the sound of cracks much more abundantly in the early morning just at sunrise. It was thought that the sun's rays shining on one side of the ice mass created a state of expansive strain. The heat of the sun was able to penetrate the ice at this hour because the ice surface was dry. The night's radiation having cooled the surface, dried up the water and from the natural tendency of a large mass of ice to maintain its inherent cold and freeze. During the day when the sun was high the whole ice surface was running with water and all the heat of the sun was continually washed away. At night the water stopped running and by midnight the surface was dry and frozen again. It was apparent that the cracking was in some way caused by sun on the dry surface and strains set up from the penetrating of the radiant energy. It may be thought absurd to ascribe any potency to rays so weak as those from the rising sun, but as familiar as the writer is to the immense influence of the very weak rays in the sky, even before sun-up on the anchor ice of the St. Lawrence where hundreds of tons of ice are brought up every morning in the water, one is no longer surprised to find an influence in this case of the sun on the dry iceberg surface. It seemed then quite reasonable to look for results from a quick application of powerful heat to the iceberg and by this means set up a heat wave in the mass to cause thermal strains. In the spring of 1926 the writer at last succeeded in arranging his own party for a trip to the east coast of Newfoundland for the purpose of applying the thermit heat units to some icebergs. This work was organized as a private venture by the writer and, apart from the courtesy of the Government of Newfoundland kindly admitting his equipment and materials free of duty, received no aid from any government.

ICEBERG EXPERIMENTS.

In all, three icebergs were treated with thermit. These were selected from 45 large bergs off the coast of Newfoundland at the twin islands of Twillingate in Notre Dame Bay. (Fig. 7.)

FIG. 7.

Twillingate harbor entrance with icebergs seen in Notre Dame Bay.

FIG. 8.

Method of landing on iceberg. This is the first one to be treated with thermit.

The first one was a large berg 500 feet long and as many wide, floating freely out at sea with cliffs rising 75 feet in the air. A long plateau enabled the writer to climb on easily with the aid of a scaling ladder and the equipment to be hoisted up with ropes. (Fig. 8.) Calked shoes and life belts served to make the sojourn on the bergs safe. A dory was used to land while a motor cruiser carried the party out to sea and remained at a short distance away

FIG. 9.

Explosion of ice due to the high temperature of 100 pounds of thermit sunk three feet jn the ice.

to watch the berg and give warning of any instability. The icebergs are of such enormous mass that they turn over very slowly and ample time is always available to get off even if one should start to turn without first giving warning by the falling off of a cliff of overhanging mass. The cruiser's whistle was the signal to retreat.

The thermit was placed in a galvanized iron container made for the purpose with lined walls. The can was sunk into the ice three feet and filled in place with thermit. It was very uncomfortably hot working on the bergs, which made it difficult to work fast. The cans were fused and when started, the party removed to the dory and then to the cruiser to watch the result

FIG. 10.

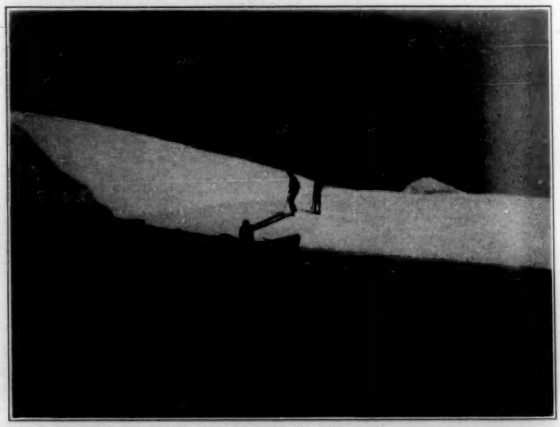
Fragments of the great plateau disrupted by the force of the explosion.

FIG. 11.

View of treated iceberg two days after, which shows great disruption.

of the shot. Only one charge of 100 pounds was placed in the first berg, but this reacted perfectly, causing a very powerful explosion of the ice, which disintegrated a great part of the large plateau. (Figs. 9 and 10.) Immediately after cracks were heard which continued all during the evening, and towards morning, about 2 o'clock, a very loud cracking awoke many people

FIG. 12.



Landing on the second iceberg in which a charge of 500 pounds of thermit was placed four feet in the mass.

in the village. On visiting the berg the next day a great part of the inside had come out between the thermit hole and the main cliffs and most of the plateau, 400 feet long, was gone. In two days the disruption thus started went on and the iceberg once so grand and firm became a poor shadow of its former self, breaking up rapidly and turning nearly completely over. No other charge was put in to complete the disruption, for the writer did not like the look of the ice and thought it more prudent to try other bergs. (Fig. 11.)

The second iceberg treated was one grounded in Jenkin's Cove in Twillingate harbor. (Fig. 12.) This was selected in order to give the people of the village a chance to see the beautiful sight of a burning iceberg. A natural ampitheatre was provided by the

FIG. 13.

Ice exploding under the fierce heat of the big thermit charge.

FIG. 14.

Disintegrated iceberg. Photo taken next morning.

high cliffs all around the cove. During the day a large charge of thermit, 500 pounds, was sunk into the ice and in the early evening just at sundown it was fired. Those who saw the spectacle will never forget the wonderful sight as the charge roared and flamed hundreds of feet into the air with the exploding ice scattering fire and sparks for hundreds of feet on either side. (Fig. 13.)

FIG. 15.

Third iceberg to be treated. Lighting the fuse for the 60-pound charge.

Vesuvius in eruption was the nearest approach to this unique sight. The effect on the ice was the same as before. The explosion disrupted a great deal of ice, but the intense heat wave cracked and honeycombed the mass and during the night and all of the next day the berg continued to fall to pieces, rolling to one side and the other as the mass was lightened by the falling pieces. (Fig. 14.) An attempt was made the next day to put a charge of high explosive on the ice to see what a sudden shock would do to the rotten ice, but a large mass fell into the sea directly in front of the dory and it was considered far from safe to venture on.

The third experiment was made on a medium-sized berg off the North Island. (Fig. 15.) This was grounded alongside of three other icebergs and from its massiveness and shape served

FIG. 16.

Explosion of ice in above iceberg. Three other bergs are seen in the distance.

FIG. 17.

Second explosion in this berg. Two charges were placed in it.

our purpose very well. It had the appearance of an inverted teacup. The ice was very hard and firm and showed no sign of disintegrating. Two charges were put off on the very peak of this berg, one of 60 pounds and the other of 100 pounds of thermit. Both charges exploded the ice (Figs. 16 and 17), but no ice was knocked off by the force of the explosion. This occurred about six o'clock in the evening. In the morning the

FIG. 18.

The next morning, iceberg was broken up entirely, only this fragment could be found floating away. The close-up shows thermit hole under water.

writer with his party visited the spot to inspect the result of the treatment, but the iceberg had disappeared and could not be found for a long time, until sufficient evidence was found that it had not floated away from the spot because a fragment was located floating in the vicinity, which contained marks of the thermit slag together with a part of the hole made for the thermit can half submerged under the water line. (Fig. 18.) This hole had been cut on the top of the berg 30 feet above the water line and been blown out funnel shaped by the explosion, easily located by this peculiar shape. The three other icebergs in this place were still in position and had not broken up. No better evidence of the peculiar nature of the heat action could be found. The writer's

party left for home that night well satisfied with the results of the experiments.

There is no question of the wonderful effectiveness of the heat treatment to control the iceberg menace for the action of the thermit heat units are most effective in the hardest and most resistant ice masses. Our experiments with high explosives verified the results obtained by the U. S. Coast Guard that they have little or no effect on these solid masses of ice. The action of the heat is quite different, it sets up the thermal expansion strain which causes innumerable cracks and fissures through which the sun and melted ice water gain access, causing the falling apart of the ice wherever the heat has been applied.

It is the author's hope that sufficient interest can be aroused to obtain means to carry out the work next year on a greater scale, because the expense of these experiments is too great for a single individual to bear in a private capacity.

No better place than Notre Dame Bay can be found for these experiments, and already plans are being made for further demonstrations, either next spring or, if funds are not forthcoming, for the following year.

THE THERMIONIC EMISSION FROM IRON-ALKALI MIXTURES USED AS CATALYSTS IN THE SYNTHESIS OF AMMONIA.*

BY

C. H. KUNSMAN, Ph.D.

U. S. Department of Agriculture, Bureau of Soils, Fixed Nitrogen Research Laboratory; Member of the Institute.

WITHIN the last few years considerable interest has been attached to certain thermionic investigations on account of the added information which may be obtained in regard to surface phenomena, mechanism of thermionic emission, ionization, adsorption, and surface catalysis. This interest was in the first place purely scientific and in the second place commercial with the application of these phenomena in the arts and industry to thermionic devices and chemical activation. Very satisfactory sources of electrons have been available in the form of high-melting metals, such as tungsten. A lower temperature source is the Wehnelt or oxide-coated surfaces and still a lower temperature source exists in the form of tungsten covered with a thin layer, probably monatomic, of thorium or an alkali metal as Cs, Rb or K.

In the case of positive charged particles or positive ions, no equally satisfactory source was available. The sources of ions usually employed were those formed under electron or cathode-ray bombardment, and were known as anode rays[1] or from heated metals, salts or coated surfaces.[2] The anode rays were subject to variations in the anode and fluctuations in the discharge, while the hot surfaces soon lost their positive-ion emitting properties and had to be reactivated in the presence of gas. Quite recently the thermal ionization of the alkali vapors in contact with sufficiently hot surfaces, such as tungsten, has been found to produce positive ions of the respective alkali metals.[3] In this case, the number of ions formed is in general a function of the nature of the hot surface, the temperature of the surface, and the vapor pressure of the alkali metal. The phenomena involved in this source of positive ions are essentially complicated and

* Communicated by the Author.

have been fertile fields for extensive researches within the past four years.

The present source of ions is of interest on account of its reliability, simplicity and ease of operation. The experimental results of these studies give further verification of certain theories as to the mechanism of thermionic emission, as well as showing some decided difference in the nature of the thermionic emission from these surfaces in comparison to those obtained from the thin condensed films. The positive-ion source was discovered in a thermionic investigation of catalysts used in the synthesis of ammonia from nitrogen and hydrogen.[4] These catalysts consist of fused artificial magnetite, to which was added about 1 per cent. of aluminum oxide and 1 per cent. of an alkali or alkaline earth metal oxide.[5] When these mixtures were mounted as the anode and heated in a vacuum tube to a dull red temperature, they were found to be copious emitters of positive ions and while the unreduced mixtures gave off some positive ions, the reduced materials gave considerably more ions.

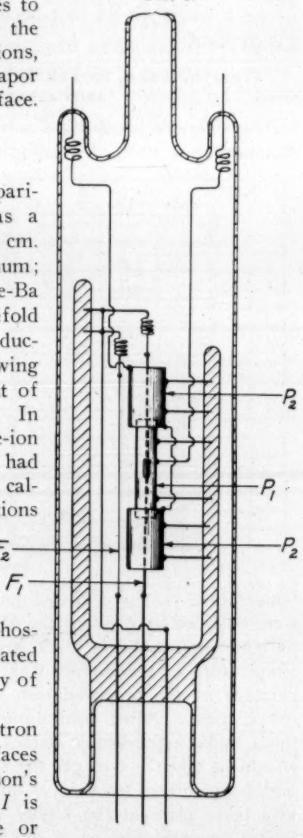
The mass spectrograph analysis of these mixtures by Barton and Harnwell at Princeton proved conclusively that the positive ions were singly charged atoms of alkali or alkaline earth metal and were very largely of the alkali or alkaline earth metal which was introduced in the original mixture.[6]

A convenient method of preparation of the anodes consisted of coating and fusing a mixture of paraffin and the finely ground granules of the oxide mixture (300 mesh or smaller) on a thin twisted platinum strip, the fusion taking place at about 900° C. in air or, preferably, an atmosphere of nitrogen. The coating process was continued until a uniform coating of the desired thickness was obtained. The coated strip was mounted as F_1 (Fig. 1), in a vacuum tube, where the oxide coating was reduced in an atmosphere of hydrogen. After a thorough baking and exhausting of the assembled Pyrex glass tube at 450° C., the collecting cylinder, P_1, and guard cylinders, P_2, were heated to about 900° C. by electron bombardment from a tungsten filament, F_2, until a pressure of 10^{-6} mm. of Hg was obtained. The temperature of the hot surface F_1 was observed by an optical pyrometer and corrections made for the emissivity of the surface and absorption of the glass. The positive and negative thermionic emission from the hot surface was measured by placing a negative

or positive saturation potential, respectively, to the collector and observing the corresponding currents on a galvanometer.

The source of ions is a part of the coating of F_1, which diffuses to the surface and vaporizes from the surface in the form of positive ions, as distinguished from gas or vapor coming from outside of the surface.

FIG. 1.



POSITIVE-ION EMISSION FROM VARIOUS SURFACES.

In Fig. 2, we have for comparison the positive-ion current as a function of the time from a sq. cm. surface for commercial platinum; Fe-Ba oxides unreduced; Fe-Ba oxides reduced, showing a fivefold increase in positive ions on reduction; and Fe-K reduced showing over 100-fold increase over that of the positive-ion current from Pt. In about two hours the positive-ion emission from the Fe mixtures had become practically constant. All calculations were made on observations obtained after a similar period of glowing in a vacuum. Observers have found that the positive ions from Pt are like those from heated aluminum phosphate and from most other heated salts, and that they consist largely of Na and K ions.[6]

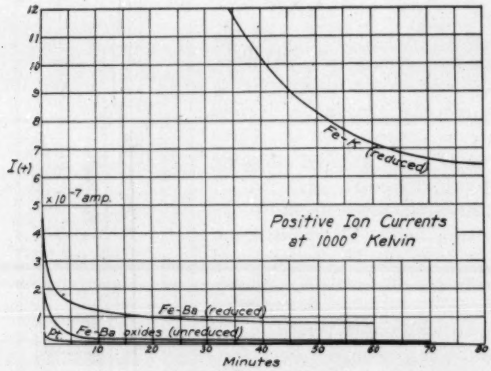
Both positive-ion and electron emission from the heated surfaces were found to obey Richardson's equation $I = AT^{\frac{1}{2}}\varepsilon^{-b/T}$, where I is the saturation current, positive or negative, T the absolute temperature, A and b constants. The A constant is usually expressed in terms of the emission per unit

surface, while the b constant will be expressed in terms of the equivalent work function of volts φ, for the vaporization of a positive ion or an electron from the surface. The relation is $b = \varphi e/k$, where e is the unit electric charge and k is the Boltzmann gas constant.

EXPERIMENTAL DETERMINATION OF φ_+ AND φ_- FROM THE IRON-ALKALI MIXTURES.

Considerable precautions need to be taken in establishing and maintaining a state of equilibrium of the surface through the

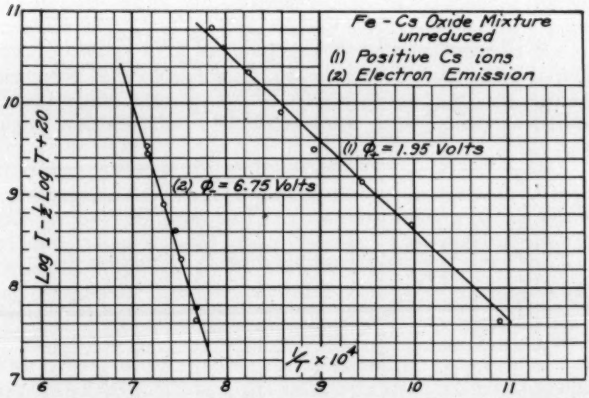
FIG. 2.



temperature range of investigation. Quite satisfactory results were obtained by glowing the filament in a vacuum for a couple of hours before taking data, and collecting positive ions as the temperature of the surface was increased to the maximum temperature of the proposed test, followed by a lowering of the temperature. After continuing with this process for a few times, quite reproducible values of φ_+ can be obtained. Care should be taken not to get the surface too hot or keep it at the high temperatures too long, as quite a rapid diminution of positive ions takes place at the higher temperatures. Likewise, at the higher temperatures, or at the limit of observations of positive ions for the φ_+ determinations, too few ions are present according to what would be expected from an extrapolation of

Richardson's equation for the lower temperatures. This is no doubt due to the lack of sufficient alkali metal atoms at the surface for vaporization. Another convenient way of taking data is to start with the surface at a somewhat lower temperature and then bring the surface to the proper temperature, observe the positive-ion current when constant, and lower the temperature. This is followed by bringing the filament up to a higher temperature until the desired temperature range is covered. If these precautions are not taken, different slopes or broken curves for a

FIG. 3.

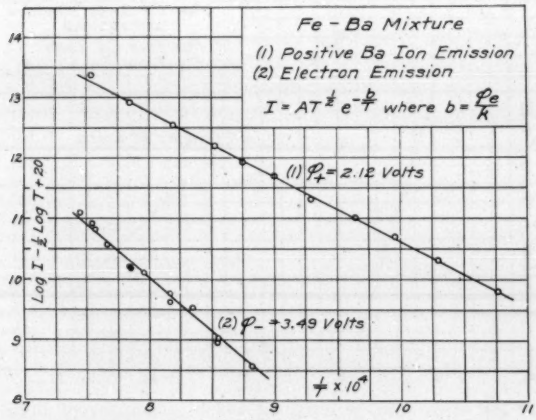


part of the range may be obtained which give apparent values of φ_+ and vary in magnitude from one to three volts, depending on the mixture and method of taking the data.

In Fig. 3, the $\log I - \frac{1}{2} \log T$ is plotted against the reciprocal of the absolute temperature, or the usual method of applying Richardson's equation. The slopes of the respective lines (1) and (2) represent the work function for a Cs ion and an electron, respectively, from an unreduced mixture of the oxides of Fe and Cs. One notices that the positive-ion emission (currents of the order of 10^{-10} amp.) starts in at a much lower temperature than the equivalent electron currents. The value of φ_- is also considerably higher than values reported for clean metal surfaces, but is not as high as the value for an oxidized tungsten surface,

9.2 volts, as reported by Kingdon.[7] That there is no marked change in the surface or value of φ_+ or φ_- through this temperature range is shown by the regularity of the observed points. Variations of the surface will be considered later. However, in general the effect of reduction of the surface by hydrogen is to increase the positive-ion emission, but keeping the slope of the curve or the corresponding value of φ_+ the same. In the case of φ_-, a general decrease to about half the original value usually takes place on reduction.

FIG. 4.



The effect of reduction of the Fe-Ba oxide surface on φ_- is seen in Fig. 4. φ_- for the reduced mixture being 3.49 volts in comparison with 6.75 volts for the unreduced Fe-Cs oxide mixture. The corresponding value of φ_+ for a single charged Ba ion is 2.12 volts.

DISCUSSION OF RESULTS.

The relative values of φ_+ and φ_- should be emphasized rather than the exact values of these functions. In an exact determination of these quantities, a method should be employed similar to one used by Davisson and Germer.[8] However, in a determination of φ_- for very pure tungsten,[9] the author obtained a value of

4.25 volts with the method as employed in the test on the Fe oxide mixtures, in comparison with 4.78 volts as determined by Davisson and Germer. The outstanding point of interest in all these curves and all others obtained to date is that in every case where φ_+ and φ_- could be measured from the same surface, φ_- was always greater than φ_+. The alkali and alkaline earth metals escape as positive ions instead of neutral metallic vapor, because the work function φ_- or the force of attraction of the surface is greater for an outer or conduction electron of the atom than the force of the atom tending to hold the electron. Either this must be true or the metal diffuses to the surface in the form of positive ions and exists there as such. Young has shown that the positive ions vaporizing from either solid or liquid pools of K or Na are negligible in comparison to the electron emission.[10] So that these surfaces must be covered with atoms and not ions. At the higher temperatures of the Fe mixture, an appreciable vaporization of Fe took place, but no iron ions were observed in the mass spectrograph studies.

It may be well to again call attention to the fact that in every case the ions emitted as tested by the mass spectrograph consisted of single atoms stripped of one electron. This was true whether the atoms were those of the alkali metals, Cs, Rb, K or Na, with one conduction or valency electron, or whether the atoms were those of the alkaline earths Ba, Sr, or Ca and Mg, having two outer conduction or valency electrons. This source of positive ions differs, therefore, from that described by Ives, in that there is no tendency to cluster. Na also leaves these surfaces as single positive charged ions instead of two joined atoms stripped of one electron as reported by Ives. Killian, however, does not find a clustering of atoms in which the cluster loses an electron, in the case of Cs, Rb and K, as shown by his current voltage curves.

The surface of these materials differs from those of the thin condensed films, in that at temperatures below the visible, in the case of a mixture containing Cs, positive Cs ions are liberated where the electron current is entirely negligible in comparison with the ion current. In the case of the thin films as reported by Ives and Becker, there are relatively few ions liberated until a considerably higher temperature is reached or until the electron emission falls off appreciably, indicating only a part of the hot tungsten surface is covered with Cs or the alkali metal. In every case, the

author has found that the ion emission is consistent in starting at a lower temperature than the electron emission (*i.e.*, currents 1×10^{-10} amp.). Likewise, no appreciable change in state is observed through the temperature range investigated, as is the case in all thin condensed film investigations.

As the phenomena involved in the emission of positive ions are a diffusion to and vaporization from the surface, it would more nearly approach the thoriated tungsten system rather than the thin condensed films. The presence of alkali and alkaline earth metal is no doubt due to a similar origin as Th from the tungsten thorium oxide filament as considered by Langmuir.[11] In the preparation of a thoriated tungsten filament, about 1 per cent. of finely divided thorium oxide is added to the tungsten oxide powder, and in the process of reduction, swedging and drawing a small amount at least of metallic thorium is produced which diffuses to the surface in the process of heat-treating the thoriated tungsten filament. On heating both the unreduced and reduced Fe-alkali oxide mixtures positive-ion emissions continue after weeks of collecting ions, showing that there is an almost inexhaustible supply of the alkali metal.

The X-ray analysis of Wyckoff and Crittenden[12] indicates that the Al and K oxides exist between the small Fe crystals. This, with the work of Geiss and Liempt,[13] who showed that diffusion takes place largely along crystal interfaces, gives us an excellent picture of where the material is largely located and how it gets to the surface.

The results on the iron-alkali mixture also indicate that there is little or no tendency for the alkali metal atoms, which have diffused to the surface, to move very far from an interface before vaporization as positive ions. Since the alkali metals vaporize more easily than thorium, there is proportionately less chance for mobility of the alkali metal atoms on surface than in the case of Th on tungsten considered by Langmuir.[11] It would seem, therefore, that the case here considered is entirely different from the case of condensed atoms on a solid surface considered by Volmer and Esterman[14] and Esterman,[15] where the absorbed atoms move over relatively large distances, 1×10^{-3} cm.

Further evidence that the alkali material does not cover an appreciable part of the Fe surface and that it is no doubt confined largely to interfaces, is that the electron emission is

negligible at the lower temperatures and that there is no experimental evidence of a low φ_- work function for these surfaces. In contrast to these results are the very large electron emissions at the lower temperatures and low values of φ_- for the electron work function, where the hot surface is assumed to be almost completely covered with an adsorbed layer of alkali metal, as reported by Langmuir, Kingdon and others.[3]

RELATION OF THERMIONIC STUDIES TO SURFACE CATALYSIS.

Results of considerable work at the Fixed Nitrogen Research Laboratory show that reduced Fe from artificial magnetite furnishes the best single element catalyst for the NH_3 reaction.[16] Likewise Fe shows a marked superiority over other elements when used as a base in connection with added substances or promoters. There is apparently some intrinsic property of iron which makes it the base of a good NH_3 catalyst.

The addition of about 1 per cent. of Al_2O_3, or another refractory oxide, increases the catalytic activity of an Fe catalyst, while the addition of about 1 per cent. of an alkali oxide further increases the catalytic activity of the mixture in the presence of Al_2O_3. This effect is especially very pronounced at the higher pressures. However, the effect of the alkali oxide on Fe alone seems to be to decrease the catalytic activity. A combination of Al and K oxide in the Fe catalyst has the effect of increasing the proportion of unsaturated or active Fe atoms as measured by the synthesis of NH_3 from N_2 and H_2.[17] We might attribute the effect of the Al_2O_3 to stabilizing the unsaturated Fe valencies by preventing sintering and crystal growth, and picture the effect of the alkali diffusing to the surface and vaporizing as volcanic in nature and keeping the surface in a state of eruption or of higher catalytic activity than would otherwise be the case. Although the effect of the alkali is very specific, the exact chemical effect on the surface is not known. It would seem reasonable that these thermionic studies may contribute toward a solution of this added catalytic effect. The interpretation of the importance of these effects is complicated by the fact that the effect of the alkali on the reduced magnetite mixture, in the absence of the aluminum oxide, shows a decreased catalytic effect over that observed on iron alone.

In the reduced catalysts, although the iron oxide is practically

all reduced to Fe, the chemical analysis shows the Al and alkali to be held in the form of the respective oxides. We shall see from the following considerations that the amount of alkali metal present is very small, and not detectable by the ordinary chemical analysis. If we take the positive-ion emission as a measure of the concentration of the alkali metal in catalyst 920 (Fe-K oxide mixture), we find at 1000° Kelvin that 1 part in 2×10^8 parts of K_2O is reduced to K and vaporizes as K ions per second. If the same rate would continue until the K_2O content was reduced to zero, the time elapsed would be about 1.3 years. This calculation no doubt gives a lower value to the concentration of the alkali as some of the alkali may escape as neutral vapor. Also the presence of H_2 increases the available alkali content for positive-ion emission. In the presence of H_2 and N_2 at 450° C., the conditions for the synthesis of NH_3, some small traces of the alkali metal must be present, although this is very small in comparison with the total alkali oxide content. Its presence on alternating the chemical or catalytic properties of the surface should not be underestimated if we can tell anything about the catalytic properties of surface from the thermionic studies of surfaces.

It has also been noticed that the presence of Al oxide tends to stabilize the positive-ion emission, which is in agreement with the idea of a double oxide, for example a K-Al oxide, which may break down to some extent on heating, liberating some K ions. Larger, but less stable, positive-ion emissions are obtained from a reduced Fe-alkali mixture which suggests that more of the alkali oxide is reduced in the absence of Al oxide, also that more of the alkali metal is available for vaporization of positive ions after reduction. Another property of the Al oxide, as pointed out by Crittenden,[12] is to stabilize or harden the catalyst structure, very similar in effect to the hardening properties of carbon in steel.

These results are the outgrowth of investigations on the possible sources of chemical activity of iron catalysts. While Al oxide fused with artificial magnetite on reduction is a good catalyst for the synthesis of ammonia, a more active one is obtained by adding about 1 per cent. of an alkali usually in the form of the nitrate, in the fusion process. It is well known that the alkali and alkaline earths are very active chemically and that very small amounts of these metals will greatly decrease the electron work

function of tungsten, or oxygen on tungsten surface, or greatly increase the electron emission at the lower temperatures. It would seem quite reasonable, therefore, that one should look for a partial explanation at least of the increased catalytic activity of an Fe, Al alkali mixture to the presence of the alkali on the surface, either in terms of an interface phenomenon, a reduction of the electron work function of the surface, the emission of positive ions with a potential or neutral vapor without a potential. Experiments in an attempt to correlate the catalytic activity of the surface measured chemically with these phenomena are under way.

CONCLUSIONS.

(1) A convenient source of positive ions of Cs, Rb, K, Na, Ba, Sr, Ca and Mg has been found.

(2) This source gives single positively charged ions under all conditions, with the absence of clustering.

(3) The source of ions is free from any marked change in the temperature of the surface (other than that predicted from Richardson's equation) in contrast to the positive ions obtained from thin condensed films.

(4) The determined values of φ_+ and φ_- for the surfaces throw further light on the mechanism of this emission. φ_+ is always less than φ_- under all conditions.

(5) The effect of reducing the mixture and surface is to decrease φ_- to about one-half the value for the unreduced surface without any appreciable change in φ_+.

(6) The probable significance of the thermionic studies in regard to surface catalysis was discussed.

The author wishes to express his appreciation for the interest shown and suggestions received in this work from the Laboratory staff; and especially to Mr. R. A. Nelson for constructing the apparatus and assisting throughout these studies.

REFERENCES.

[1] DEMPSTER: *Phys. Rev.*, **11**, 316 (1918); **18**, 415 (1921).
ASTON: *Phil. Mag.*, **42**, 436 (1921).
[2] O. W. RICHARDSON: "Emission of Electricity from Hot Bodies," 2d ed., Chap. 6-8.
[3] LANGMUIR and KINGDON: *Science*, **57**, 58 (1923); *Phys. Rev.*, **21**, 380 (1923); *Proc. Roy. Soc.*, **A107**, 61 (1925).
IVES: *Phys. Rev.*, **15**, 102 (1922); JOUR. FRANK. INST., **201**, 47 (1926).
KILLIAN: *Phys. Rev.*, **27**, 578 (1926).
BECKER: *Phys. Rev.*, **28**, 341 (1926).

[4] KUNSMAN: *Phys. Rev.*, **25**, 892 (1925); *Science*, **62**, 269 (1925); *J. Phys. Chem.*, **30**, 525 (1926); *Phys. Rev.*, **27**, 249 (1926); *Science*, **63**, 483 (1926).
[5] LARSON and RICHARDSON: *J. Ind. Eng. Chem.*, **17**, 971 (1925).
[6] BARTON, HARNWELL and KUNSMAN: *Phys. Rev.*, **27**, 739 (1926).
[7] KINGDON: *Phys. Rev.*, **23**, 774 (1924).
[8] DAVISSON and GERMER: *Phys. Rev.*, **20**, 300 (1922); **24**, 666 (1924).
[9] Furnished through the courtesy of Dr. I. Langmuir of the Gen. Elec. Co.
[10] YOUNG: *Proc. Roy. Soc.*, **A104**, 611 (1923).
[11] LANGMUIR: *Phys. Rev.*, **22**, 357 (1923).
[12] WYCKOFF and CRITTENDEN: *J. Am. Chem. Soc.*, **47**, 2866 (1925).
[13] GEISS and LIEMPT: *Z. Metallkunde*, **16**, 317 (1924).
[14] VOLMER and ESTERMAN: *Zeit. f. Physik.*, **7**, 13 (1921).
[15] ESTERMAN: *Zeit. f. Physik.*, **33**, 320 (1925).
[16] ALMQUIST and CRITTENDEN: *Jour. Ind. Eng. Chem.*, **18**, 1307 (1926).
[17] ALMQUIST: *Jour. Am. Chem. Soc.*, **48**, 2820 (1926).

WASHINGTON, D. C.
October 11, 1926.

THE DISCRIMINATION OF THE QUALITY OF BRICK BY MEANS OF SOUND.*

BY

JÛICHI OBATA.

Physics Division, Aeronautical Research Institute, Tokyo Imperial University.

In discriminating the quality of material the sound produced by striking it is very often utilized in practice. In the case of brick it is generally believed that one which gives a metallic sound when struck by a hammer has superior quality as the architectural material, and this opinion is undoubtedly correct.

The present author has recently had an opportunity to investigate the problem systematically so as to find the relation between the quality of brick and the sound produced by striking. As the results are believed to be of some value in discriminating similar kinds of materials, it will be briefly given here.

About thirty specimens, which were selected among several hundred similar ones, have been tested, the majority of them being the overburnt. The specimen has a length of about 23 cm. and a square cross-section of about 5×5 cm., and to produce sound it was supported by the hand and struck at the middle part with a small steel hammer.

It was undertaken at the outset to obtain the record of sound by means of a Low-Hilger Audiometer, which has been recently put on the market by Adam-Hilger, Ltd., London. Owing, however, to the low natural frequency and small damping of the membrane used in the instrument, it was found impossible to obtain a record of such a momentary sound with it.

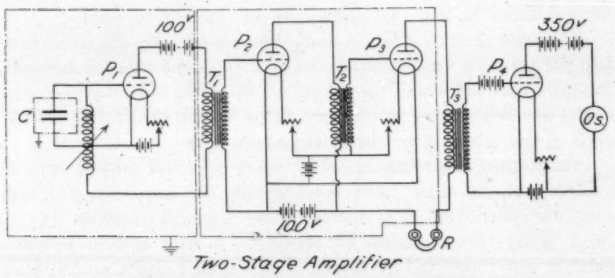
A condenser microphone was therefore employed, the record being obtained with an oscillograph made by the Cambridge Instrument Company, England. The electrical connection is shown in Fig. 1. The condenser microphone was constructed in the workshop of our laboratory and was the same as that used in the previous experiments, a thin sheet of German silver, thickness 0.05 mm., stretched tightly, being employed as the membrane.

As shown in Fig. 1, transformer couplings were employed

* Communicated by the Author.

throughout for the sake of simplicity, so that the record may not be accurate, if the utmost degree of precision is aimed at, though it was quite satisfactory for the present purpose. In order to test the degree of distortion caused by the recording system, a pair of telephone receivers was inserted as shown in the figure, and long lead wires attached to the receiver; the sound of brick was heard in a distant room through the recording system and was compared with that heard directly with unaided ears. Two specimens were selected, which were at the two extremes as regards the pitch of sound; namely, the one produced a sharp metallic

FIG. 1.



C—Condenser microphone. *P*₂ and *P*₃—Cymotron 201.
OS—Oscillograph. *P*₄—Cymotron 202.
P—Marconi valve *Q*. *R*—Telephone receiver.
Electrical connection of the recording system.

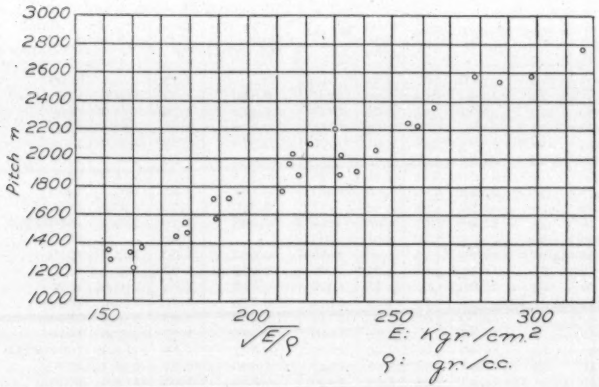
sound and the other gave a dull damped sound. These two specimens were struck alternately and the difference in the sharpness of sound was compared, *i.e.*, heard with unaided ears or with receivers through the recording system. Owing to the use of transformers and also of the telephone receiver, the difference in the sharpness of sound was somewhat less remarkable when heard through the recording system than when heard directly; it may be accounted for by the suppression of higher partials by the recording system.

Records of sound were obtained with about thirty specimens, some of which are reproduced in Fig. 4. A wave of 50-cycle alternating current was recorded simultaneously as the timing wave.

In the beginning of the work it was soon noticed that there

existed remarkable difference in the degree of damping of the sound in various specimens, and it was hoped that by the oscillographic record of the sound produced, the pitch as well as the degree of damping of the sound might be accurately determined, both being believed to have an intimate relation to the quality of the material. As a matter of fact, it was, however, found that in some specimens the intensity of sound was greatest in the beginning and then gradually died out, while in others, the sound

FIG. 2.



Relation between the pitch and $\sqrt{E/\rho}$.

attained its maximum after an elapse of some time.[1] Moreover, a beautiful beat was observed with some specimens.

To produce sound the specimen was simply supported with the left hand and struck at the middle part with a small steel hammer held in the right hand. The force of the blow as well as the speed of separation of the hammer after striking may not be constant in each case, so that the complex nature of the sound may be due partly to the difference in the mode of striking. Anyhow, owing to such complex nature of the sound the comparison of the degree of damping was made somewhat difficult, and hence only the pitch was determined from the record.

[1] A similar phenomenon was observed by Dayton C. Miller upon the tone of a piano, "The Science of Musical Sound," 1922, p. 209.

After finishing the recording of sound, a compression test was made upon the majority of the specimens in the Material Testing Division in our Institute under the direction of Prof. T. Inokuty, and Young's modulus was determined.

The dimensions, weight, pitch n, density ρ and Young's modulus E of the specimens are given in Table I.

In the last column are given the values of pitch which are calculated with the dimensions and Young's modulus according to

TABLE I.

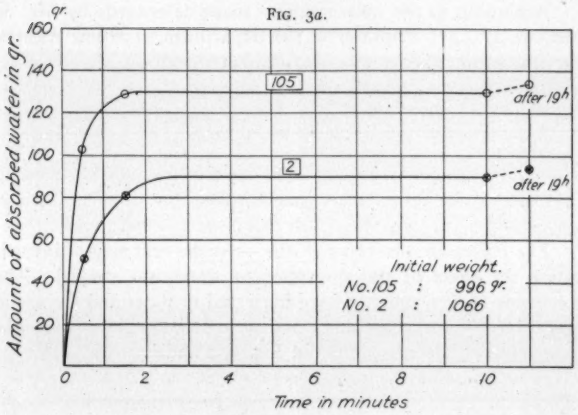
Specimen No.	Film No.	Length. cm.	Width. cm.	Thickness. cm.	Weight. gr.	Young's Modulus $E/10^6$. [kgr./cm².]	Density. ρ	$\sqrt{E/\rho}$	Pitch. (Obs.)	Pitch. (Calc.)
305	2	23.16	5.00	4.75	973	.....	1.77	.....	1100	
373	20	22.59	5.03	5.00	1147	0.440	1.72	160.0	1230	1667
289	21	22.53	5.03	5.05	1024	0.422	1.79	153.6	1290	
366	32	23.29	5.05	4.95	1053	0.468	1.81	159.1	1340	
374	18	23.25	5.06	4.91	970	0.379	1.67	150.6	1360	
270	19	23.05	5.08	5.00	957	0.432	1.63	162.6	1380	1558
390	3	23.05	5.11	4.98	966	0.531	1.70	174.8	1450	
375	31	23.25	5.00	5.00	1052	0.581	1.81	179.2	1480	
386	16	22.78	5.05	4.94	977	0.540	1.70	178.2	1550	
120	33	22.95	4.91	4.86	929	0.608	1.70	189.4	1580	1776
378	30	22.75	5.10	5.08	993	.....	1.68	.....	1680	
105	54 or 6	22.89	4.93	4.98	1036	0.652	1.85	187.8	1710	
78	17	22.85	4.98	4.85	1006	0.677	1.82	192.7	1720	
70	24	22.66	5.07	4.88	1029	0.816	1.84	210.9	1770	
357	48 or 23	23.06	5.12	5.01	1103	0.876	1.86	216.8	1890	
82	22	22.60	5.06	5.03	1044	0.968	1.82	230.9	1890	
351	7	22.85	5.09	5.09	1046	0.995	1.77	237.0	1910	
298	29	22.09	5.09	4.99	1009	0.827	1.80	214.4	1960	2231
148	43	22.62	4.95	5.01	1047	1.006	1.87	232.2	2020	
346	35 or 10	22.43	5.05	5.03	1040	0.843	1.83	214.9	2030	
297	28	22.00	5.12	5.07	1046	1.091	1.83	244.0	2060	
304	13	22.45	4.91	5.00	1045	0.924	1.90	220.7	2100	
299	25	21.93	5.07	5.05	1022	0.986	1.82	230.1	2210	
326	34	22.26	4.93	5.06	1085	1.298	1.95	257.7	2230	
33	14	22.35	5.07	5.10	1081	1.212	1.87	254.6	2250	2645*
350	15	22.64	5.08	5.03	1069	1.290	1.85	264.3	2360	
26	4	21.96	5.03	5.00	979	1.490	1.81	286.6	2540	
20	50	21.95	5.07	5.05	1005	1.381	1.79	278.0	2580	2964
307	5	22.59	5.03	5.00	1147	1.788	2.02	297.7	2590	
2	53 or 8	21.93	5.07	5.04	1072	1.914	1.91	316.3	2770	3373

* Upon this specimen a tension test was also made, as the result of which it is found $E_T = 0.962 \times 10^6$ kgr./cm²., and using this value of E the calculated pitch becomes 2356.

the theory of transverse vibration of a bar, assuming the specimen to be a thin free-free bar.

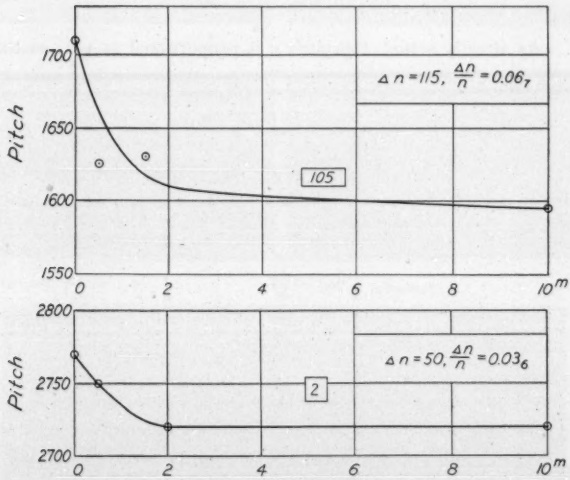
The relation between the pitch n and $\sqrt{\frac{E}{\rho}}$ is plotted in Fig. 2, a linear relation being found as expected theoretically.

FIG. 3a.



Increase in weight.

FIG. 3b.



Lowering of pitch.

According to the measurements made afterwards by Mr. S. Kanamori,[2] Civil Engineer to the Department of Home Affairs, the following relation was obtained between the pitch and compressive strength of brick:

$$\text{Compressive strength (in lb. per sq. in.)} = \frac{100}{35} \cdot n - 1500,$$

where n is the pitch of sound. The value of compressive strength calculated by means of this equation, using the value of pitch n, agrees within ± 30 pounds with that actually determined.

The Effect of Absorbing Water.—As the next step of investigation the effect of the absorption of water was studied. The specimens Nos. 2 and 105 were immersed in water and the sound was recorded at various times, measuring the weight at the same time. The results are plotted in Fig. 3, *a* and *b*.

It will be seen from these results that the water is absorbed rapidly in the beginning and in consequence the pitch of sound decreases at an equally rapid rate, and after the lapse of only a couple of minutes the absorption reaches saturation and the pitch attains a constant value.

As already stated, the pitch n is proportional to $\sqrt{\frac{E}{\rho}}$, so that we have,

$$\frac{\triangle n}{n} = \frac{1}{2}\frac{\triangle E}{E} - \frac{1}{2}\frac{\triangle \rho}{\rho}.$$

From the results shown in Fig. 3, the change in pitch $\triangle n/n$ and that in density $\triangle \rho/\rho$, due to the absorption of water, were obtained and are shown in the following table:

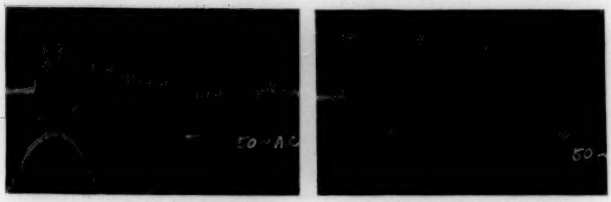
Specimen.	$\frac{\triangle n}{n}$.	$\frac{1}{2}\frac{\triangle \rho}{\rho}$.
105	0.067	0.065
2	0.036	0.042

It will be seen from this table that the change in pitch caused by the absorption of water may be entirely accounted for by the

[2] The present work was undertaken according to the proposal of Mr. S. Kanamori.

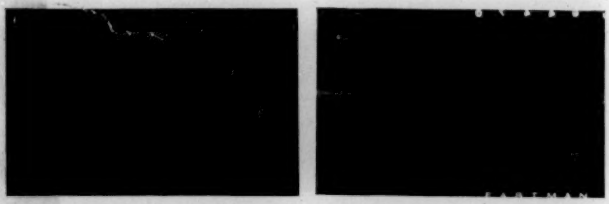
FIG. 4.

Specimen No. 373. $n = 1230$. Specimen No. 289. $n = 1290$.

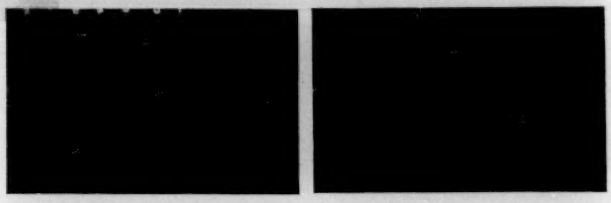


→ Time → Time

Specimen No. 366. $n = 1340$. Specimen No. 390. $n = 1450$.



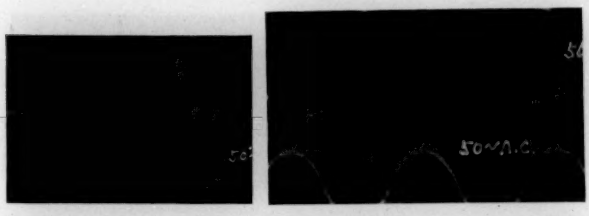
Specimen No. 375. $n = 1480$. Specimen No. 120. $n = 1580$.



Specimen No. 70. → Time $n = 1770$.

FIG. 4 (*Continued*).

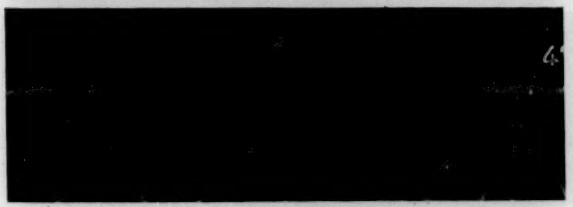
Specimen No. 378. $n=1680$. Specimen No. 105. $n=1710$.



→ Time

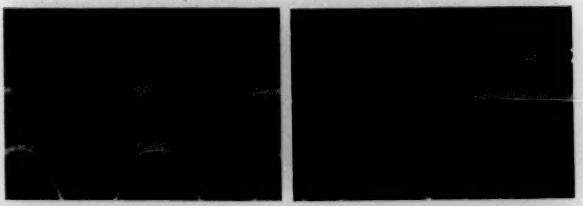
Specimen No. 105. After immersing nineteen hours in water. → Time $n=1615$.

Specimen No. 357. Direction of blow "*aa*." $n=1870$.



→ Time

Specimen No. 357. $n=1910$. Specimen No. 82. $n=1890$.



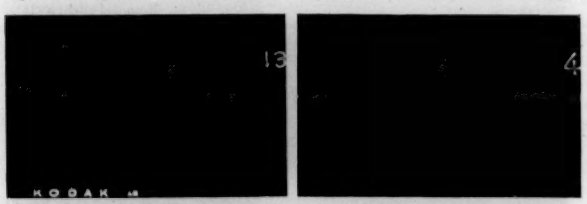
Direction of blow "*bb*."

FIG. 4 (*Continued*).

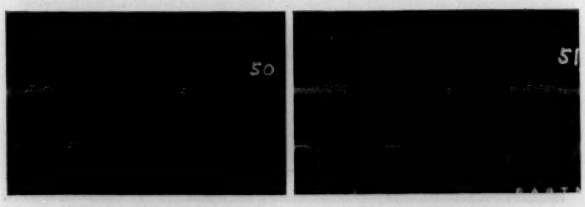
Specimen No. 148. $n = 2020$. Specimen No. 297. $n = 2060$.

Specimen No. 299. → Time $n = 2210$.

Specimen No. 304. $n = 2100$. Specimen No. 26. $n = 2540$.



Specimen No. 20. $n = 2610$. Specimen No. 20. $n = 2490$.



Direction of blow "*aa*." Direction of blow "*bb*."

FIG. 4 (*Continued*).

Specimen No. 2. → Time $n=2770$.

Specimen No. 2. $n=2720$.

After ten minutes immersing in water.

FIG. 5*a*.

Xylophone. Recorded pitch: $n=1070$.

Xylophone. $n=1460$.

FIG. 5*a* (*Continued*).

Xylophone.

FIG. 5*b*.

Galton whistle c^3(1035). Recorded pitch: $n=1000$.

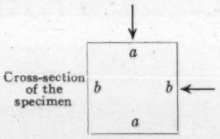
Galton whistle g^3(1550). Recorded pitch: $n=1590$.

change in density and not by the change in Young's modulus, which is a fact also anticipated.

The Beat.—As already mentioned, a beautiful beat is often observed in the record of sound of brick, the reason of which may easily be explained. The specimen has a square cross-section 5×5 cm. Inevitably there may, however, exist a slight difference in the length of sides of the cross-section, *i.e.*, in the thickness of the rod in the two directions. When one of the surfaces of the specimen is struck, the vibration in the direction parallel to the surface may also occur, which gives rise to a sound of slightly

different pitch owing to the slight difference in the thickness in the two directions, perpendicular and parallel to the struck surface. The sound interferes with the principal one and produces a beat.

In order to test this view, each of these two sounds was recorded upon two specimens, which gave remarkable beats, and the pitches were determined. As shown in the following table, the difference in pitch agrees very well with the number of beats per second estimated from the record; the above view being thus confirmed.



Specimen No.	Film No.	Direction of Blow.	Thickness in cm.	Pitch.	Difference in Pitch.
357	47	*a a*	5.01	1870	40
357	48	*b b*	5.12	1910	No. of beat estimated by the Film 47: 54 per second.
20	50	*a a*	5.07	2610	120
20	51	*b b*	5.05	2490	No. of beat estimated by the Film 50: 118 per second.

Records of Other Sounds.—When discriminating a large number of brick in practical work, a standard instrument of sound is in all cases necessary, with which the sound of brick is compared with unaided ears and the approximate pitch is estimated. A tuning-fork is not suited for this purpose, because its tone color is much different compared with that of brick. It was found by Mr. S. Kanamori that the tone of a xylophone was most suitable for the purpose. A few records of the tones of a xylophone were therefore obtained in a similar manner and reproduced in Fig. 5*a*. The general appearance resembles very well that of the sound of brick. Finally, tones of a Galton whistle made by

Edelmann and Son, Germany, were recorded for the sake of reference (Fig. 5*b*).

In conclusion, mention must be made of the peculiar nature of the sound of brick as well as the tone of a xylophone. They give a feeling of sounds about two octaves lower than those determined by the oscillographic records, while in the case of brick the pitch obtained by the records agrees fairly well with those calculated with the dimensions and the values of Young's modulus of the specimens. Further investigations will be made in the future on this point.

The Sun, the Earth's Atmosphere and Radio Transmission. S. CHAPMAN. (*Nature,* March 19, 1927.)—A generation ago it is unlikely that any one would have considered of importance to the human race day by day the condition of the atmosphere twenty-five or more miles above the earth. The prevalence of radio transmission has made this distant region of the atmosphere of significance. An electric wave travels slantingly upwards and reaches an ionized layer at a considerable height. Its direction of advance is there changed so that it is deflected downwards and some of the energy of the wave is absorbed at the same time. How do the upper reaches of the atmosphere acquire their ions? Perhaps to some extent by the action of the penetrating radiation of Kohlhoerster and Milligan and of the errant electrons developed, according to C. T. R. Wilson, in thunderstorms, but these two influences are trivial in comparison with the effect of the sun, which intervenes in two ways. The ultra-violet radiation from the sun is absorbed in the upper air chiefly by the ozone which itself is due to the action of the same radiation. Thereby ions are produced and the layer where they abound becomes electrically conducting. This effect is, of course, limited to that hemisphere of the earth on which the sun is shining. By the rotation of the earth this layer is carried into the shadow. The ions proceed to re-combine. This is most rapid at the lower surface of the layer, so that with the passage of time the lower boundary of the layer rises, in a few hours ascending 50 km. At night, therefore, the conductivity of the ionized layer is less than by day for two reasons, its thickness is less and there are fewer ions present. Thus the strength of the electrical currents in the layer is reduced. To them is attributed the daily variations in the terrestrial magnetic field, which are more considerable by day than at night and in equatorial regions than in higher latitudes.

The second solar influence is due to a bombardment of the upper air by corpuscles coming from the sun, especially from locally disturbed areas on that body. These penetrate to an elevation of 80 km. above the earth. Being charged electrically they are deflected by the earth's magnetic field toward the magnetic poles and produce effects on both the day and night sides of the earth. They appear not regularly but fitfully and produce auroras and magnetic storms. If they are emitted by a sun-spot their effects are likely to recur after an interval of twenty-seven days, *i.e.,* after the sun has rotated once on its axis.

Improved conditions of radio transmission at night are explicable by changes in the conducting layer caused by ultra-violet light. It has been observed that transmission from Europe to North America is more likely to grow bad than from Europe to the East. This has to do with the concentration of corpuscles about the north magnetic pole of the earth in northern Canada. G. F. S.

STATISTICAL MECHANICS AND ITS APPLICATION TO PHYSICAL-CHEMICAL PROBLEMS.

BY

RICHARD C. TOLMAN, Ph.D.

Professor of Physical Chemistry and Mathematical Physics, California Institute of Technology.

LECTURE II.—SOME APPLICATIONS OF STATISTICAL MECHANICS TO SYSTEMS THAT ARE IN EQUILIBRIUM.*

BARTOL RESEARCH FOUNDATION

Communication No. 12.

(1) *Introduction.*—At the end of the last lecture we concluded that it seemed reasonable to take a microcanonical ensemble of systems distributed uniformly in the phase space with energies between E and $E + dE$, as giving a fair representation of the successive states of a single system left to itself with energy in that range. This principle provides the basis for nearly all the results of statistical mechanics which have practical application to systems of molecules, and in the present lecture I wish to describe to you some of the results which we obtain in this manner for systems of molecules that are in a steady condition of equilibrium. The results are so numerous and the time available so short that I shall have to omit a great many, and even then I am afraid that my lecture may sound too much like a page of equations read out from a handbook of mathematics.

(2) *The Maxwell-Boltzmann Distribution Law.*—The first result of statistical mechanics to which I wish to call your attention is the well-known Maxwell-Boltzmann distribution law. Consider a gas containing N molecules, and let the condition of each molecule be specifiable by giving the values of n generalized coördinates and the corresponding momenta $q_1 \ldots p_n$. Three of these coördinates, say q_1, q_2, and q_3, could be taken as the three coördinates x, y, and z which give the position of the centre of gravity of the molecule and the corresponding momenta, p_1, p_2, and p_3 would then be the linear momenta $m(dx/dt)$, $m(dy/dt)$ and $m(dz/dt)$, where m is the mass of the molecule. The remaining coördinates $q_4 \ldots q_n$ could then be used to specify the angular orientation of the molecule and the positions of its internal parts, and the corresponding momenta $p_4 \ldots p_n$ deter-

* Delivered in the lecture hall of the Institute, Friday afternoon, November 19, 1926.

mined by the equation of definition connecting momenta with the Lagrangian function.

If we have a gas consisting of such molecules, it is evident that different molecules can assume widely different values of these coördinates and momenta; some may be in one part of the vessel and some in another, some moving rapidly and some slowly, some with large internal energies and others with small. Nevertheless, it can be shown, by considering the microcanonical ensemble which corresponds to our gas, that almost every sample of gas in that ensemble will have a distribution of the molecules which does not differ appreciably from that given by the equation

$$dN = NCe^{-\frac{\varepsilon}{kT}} dq_1 \cdots dp_n \tag{1}$$

where dN is the number of molecules whose coördinates and momenta fall in the range $dq_1 \ldots dp_n$, ε is the energy that a molecule has with these values of coördinates and momenta, k is Boltzmann's constant, T is the absolute temperature, and C is a parameter which depends only on the temperature and the structure of the molecule involved. Since the integration of the expression given by equation (1) over all possible values of the q's and p's must give the total number of molecules N, it is evident that the value of C is given by the equation

$$C = \frac{1}{\int \cdots \int e^{-\frac{\varepsilon}{kT}} dq_1 \cdots dp_n}. \tag{2}$$

The number of problems that can be treated merely by applying the Maxwell-Boltzmann distribution law is perfectly astounding.

(3) *The Maxwell Distribution Law.*—First of all we may note that Maxwell's law for the distribution of velocities among the molecules of a gas is of course merely a special case of the more general equation (1). Providing we can divide the energy ε of the molecule into two parts, its kinetic energy as a whole and a remainder which I shall call ε_i, we can evidently rewrite equation (1) in the form

$$dN = NCe^{-\frac{\varepsilon_i + \frac{m}{2}(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)}{kT}} dx\,dy\,dz\,m^3 d\dot{x}\,d\dot{y}\,d\dot{z}\,dq_4 \cdots dp_n dp_4 \cdots dp_n \tag{3}$$

and, by integration over all values of x, y, z and $q_1 \ldots q_n$ $p_1 \ldots p_n$, obtain

$$dN = NC'e^{-\frac{m}{2kT}(\dot{x}^2+\dot{y}^2+\dot{z}^2)}\,d\dot{x}\,d\dot{y}\,d\dot{z} \qquad (4)$$

where dN is now the number of molecules whose component velocities lie in the range $d\dot{x}\,d\dot{y}\,d\dot{z}$, and C' can evidently be shown to have the value

$$C' = \frac{1}{\iiint e^{-\frac{m}{2kT}(\dot{x}^2+\dot{y}^2+\dot{z}^2)}\,d\dot{x}\,d\dot{y}\,d\dot{z}}. \qquad (5)$$

(4) *Collisions with Walls and between Molecules.*—Knowing the way the velocities are distributed among the different molecules, we can now easily calculate the number of collisions with the walls and thus determine the momentum transferred per second to the walls and account for the pressure of the gas by methods that are familiar to you.

We can also investigate the number of collisions between the molecules themselves. The computations are somewhat lengthy, but as you know, assuming the molecules to be rigid elastic spheres of a given diameter, we can finally obtain expressions for the number of collisions per second between molecules of the same or different kinds at any desired concentration and temperature. Also, a fact which may be less familiar, we can obtain expressions for the number of collisions in which the relative velocity of the two colliding molecules lies in any given range,[1] and for the number of collisions in which the "head-on" component of this relative velocity lies in a given range.[2] These results have been of immense importance in assisting the chemist to determine whether molecules could be chemically activated by collision, the *apparent* result being that they cannot, as we shall later see.

(5) *Averages from the Maxwell-Boltzmann Law.*—Returning now to the general form of the Maxwell-Boltzmann law as given by equation (1), it is evident that we can use it for determining the average value for any property P of the molecules.

[1] JEANS, "Dynamical Theory of Gases."

[2] LANGEVIN and RERY, *Le Radium*, 10, 142 (1913).

To do this we merely have to multiply the number of molecules dN in any state by the value of P in that state, add together for all states, and divide by the total number of molecules N, giving us

$$P_{\text{av.}} = \frac{1}{N} \int \cdots \int NCe^{-\frac{\varepsilon}{kT}} P dq_1 \cdots dp_n \tag{6}$$

where P is to be regarded as a function of the coördinates and momenta $q_1 \ldots p_n$ which determine the state of a molecule.

I wish to consider with you only one result of this fundamental equation, which arises when the energy ε can be given as a sum which contains one or more terms which are dependent on a single coördinate or momentum. Under these circumstances it is easy to show with the help of a partial integration that we shall have for each such coördinate q_i or momentum p_j the general result [3]

$$\left[q_i \frac{\partial \varepsilon}{\partial q_i}\right]_{\text{av.}} = \left[p_j \frac{\partial \varepsilon}{\partial p_j}\right]_{\text{av.}} = \cdots = kT. \tag{7}$$

This very beautiful relation may be called the *general equipartition law,* and holds in cases where the more familiar principle of the equipartition of energy breaks down completely. Only when the energy is proportional to the square of the coördinate or momentum in question, as, for example, in the case of the ordinary kinetic energy of a molecule

$$\varepsilon_j = \frac{m}{2} \dot{q}^2_j = \frac{1}{2m} (m\dot{q}_j)^2 = \frac{1}{2m} p^2_j, \tag{8}$$

does the general principle reduce, as you will see by substitution in equation (7), to the equipartition of energy

$$\bar{\varepsilon}_j = \frac{1}{2} kT, \tag{9}$$

or considering all three directions

$$\bar{\varepsilon}_{\text{kin.}} = \frac{3}{2} kT.$$

Thus in relativity mechanics where the simple expression for

[3] See TOLMAN, *Phys. Rev.*, **9**, 261 (1918). The result is dependent on the assumption that ϵ, q_i and p_j have certain values at the limits of integration. This assumption, however, is met by the systems of usual interest.

kinetic energy given by equation (8) is no longer exact, we find that the average kinetic energy of a molecule at low temperatures is given by a series

$$\bar{\varepsilon}_{\text{kin.}} = \frac{3}{2} kT + \frac{15}{8m}\left(\frac{kT}{c}\right)^2 + \cdots \qquad (10)$$

and for very high temperatures or very small masses this becomes

$$\bar{\varepsilon}_{\text{kin.}} = 3kT \qquad (11)$$

instead of $3/2\ kT$.

I call your attention to this fact to emphasize the dangers of a too naïve application of the principle of the equipartition of energy, even in those fields where quantum restrictions do not enter.

(6) *Modifications Introduced by the Quantum Theory.*—We must now turn our attention to the modifications that must be introduced into statistical mechanics to take account of quantum theory. The really correct nature of these modifications will only become certain when the new quantum dynamics itself becomes certain. At the present moment, however, this is far from the case. In the hands of Heisenberg, Born and Schrödinger the new dynamics changes over night and last week's results are already ancient history. Under the circumstances it is impossible for us to wait the long time that may perhaps elapse before the new dynamics has reached its final form, and the even longer time that will certainly elapse before most of us will be able to understand the outcome. We must compromise by taking quantum theory in the form which it received from the hands of Bohr and Sommerfeld, and tentatively introducing into statistical mechanics those modifications that seem to be indicated.

For our purposes the quantum phenomena of first interest are the definite quantized states in which atoms and molecules appear to spend, at least all but a very fleeting portion of their existence. In contradiction to our experience with mechanical systems of macroscopic size which appear to take up or give out energy in continuous amounts, atoms and molecules, and presumably other systems where high frequencies are involved, appear to be endowed with definite energy levels, and must pick up their energy in finite amounts, when they pass from any level to a

higher one. Those experiments, in which we bombard atoms with electrons of different velocities and obtain none but elastic collisions until the electrons are given sufficient energy to raise the atom to its next higher energy level, seem alone to provide almost inescapable evidence for the real existence of these quantum states.

This fact must immediately modify the fundamental basis of our statistical mechanical considerations. The concept of a microcanonical ensemble with phase points uniformly distributed in the region of the γ-space included between the surfaces of constant energy between E and $E + dE$, and moving as determined by the classical laws of motion, can now be regarded only as a first approximation. In the first place, the γ-points must actually be distributed not uniformly, but on those surfaces in the phase space which will put all the molecules in their allowed quantized states. In the second place, as time proceeds, the phase point for a given system must on occasion jump from one of these allowed surfaces to another in a manner not contemplated when we applied the Hamiltonian equations of motion to determine the behavior of these points. Under the circumstances, especially since we have no theory of the laws governing the actual motion of the phase point when it jumps from one allowed state to another, we are in a very difficult situation.

As a basis for proceeding, and we must proceed if we wish to apply statistical mechanics to anything but molecular velocities or other motions of such low frequency that we can still trust the classical mechanics, only a single hint is given us. This hint we must grasp tentatively but boldly; develop its consequences and subject the results to the test of experiment. I may remark in advance that the outcome of these tests is at least sufficient to make us believe that we are apparently on the right track.

The hint in question is contained in the very rules of quantization themselves. If we consider the 2-m dimensional phase space that we have used for plotting the coördinates and momenta $Q_1 \ldots P_m$ for our system, then on the basis of the classical theory the phase point of our system could assume a continuous range of positions in this space. On the basis of the quantum theory, on the other hand, the phase point can only lie on definite surfaces corresponding to the different quantum states. The rules of quantization, however, are such that we find that these surfaces divide the whole phase space into cells of equal volume

h^s, where h is Planck's constant and s is the number of degrees of freedom of the system. Furthermore these cells are so arranged that we can regard each particular cell as belonging to a particular permitted state.[4] Hence it seems reasonable to assign to each permitted state the volume of its corresponding cell, in spite of the fact that the phase point cannot, as in the classical theory, remain in the interior of the cell.

Returning now to our microcanonical ensemble, we see that all the phase space between the surfaces of constant energy E and $E + dE$ is now assigned to definite states of the system, just as in the classical theory, and we may proceed as we did before. To determine the probability of finding our system at an arbitrary time in any given condition, we shall merely have to examine our microcanonical ensemble and determine how large is the volume of phase space that corresponds to this condition. And if we find that practically the whole volume of phase space corresponds to some particular molecular distribution, we shall expect to find that this distribution is the one which the molecules will actually assume at equilibrium.

(7) *Maxwell-Boltzmann Distribution Law as Modified by Quantum Theory.*—I am afraid that this description of the way we introduce quantum theory into statistical mechanics has sounded arbitrary and vague. As to its arbitrariness I can make no apology. The method of introduction is arbitrary and can only be justified by its results. For the present we have to follow a sort of "hunch" and only when we get a more complete quantum mechanics will we be able to introduce quantum theory in a less arbitrary fashion. As to the vagueness, however, I assure you that this arises only from the impossibility of being more specific in so short a time.

Perhaps I can best convince you of the specificity of the modification introduced by giving you one of its very specific results, namely, the modified form which we now find for the Maxwell-Boltzmann distribution law

$$N_i = NCe^{-\frac{\varepsilon_i}{kT}} h^n, \qquad (12)$$

where N_i is the number of molecules at equilibrium in the ith quantum state, the energy in that state being ε_i. This equation

[4] Certain complications sometimes arise which we need not now discuss.

you see is entirely analogous to our original equation (1) for the classical case. The only difference is that the continuously variable energy ε of the classical mechanics is replaced by the definite energy ε_i of the given quantum state, and the infinitesimal volume in the μ-space $dq_1 \ldots dp_n$ is replaced by the finite volume h^n, where h is Planck's constant. Since h has the dimensions of $q \times p$, the volume h^n has the same dimensions as does $dq_1 \ldots dp_n$.

The constant C can be determined as before by the condition that the summation of (12) for all quantum states must give us the total number of molecules N, and this evidently leads to the result

$$C = \frac{1}{\sum_i e^{-\frac{\varepsilon_i}{kT}} h^n} \tag{13}$$

and by division we can cancel out the factor h^n and write the more convenient expressions

$$N_i = \frac{Ne^{-\frac{\varepsilon_i}{kT}}}{\sum_i e^{-\frac{\varepsilon_i}{kT}}} = \frac{Np_i e^{-\frac{\varepsilon_i}{kT}}}{\sum_i p_i e^{-\frac{\varepsilon_i}{kT}}}, \tag{14}$$

where the second form containing p_i may be used if we desire, in the case of so-called degenerate systems, to group together p_i separate quantum states which happen to have the same energy ε_i.

Oftentimes we wish to treat some of the degrees of freedom of a molecule in accordance with the classical theory and some in accordance with quantum theory. Thus the three translational degrees of freedom for a molecule in a dilute gas can evidently be treated classically, while the internal degrees of freedom must in general be treated in accordance with the quantum theory. Under these circumstances, if we have r classical degrees of freedom and s quantized degrees of freedom, we can use a mixed expression of the form

$$dN_i = \frac{\left(Ne^{-\frac{\varepsilon_i}{kT}} h^s\right) e^{-\frac{\varepsilon}{kT}} dq_1 \cdots dp_r}{\left(\sum_i e^{-\frac{\varepsilon_i}{kT}} h^s\right) \int \cdots \int e^{-\frac{\varepsilon}{kT}} dq_1 \cdots dp_r}. \tag{15}$$

I realize that this equation may seem to you a monster of abortion, containing as it seems disparate elements taken from both theories. Perhaps the matter will be elucidated if I call your attention to the fact that the successive quantum states for the degrees of freedom that we can treat as classical must have energy contents which do not differ appreciably one from another. Hence the infinitesimal volume of phase space $dq_1 \ldots dp_r$ can be taken small enough so as to correspond to a definite value of ε, and yet be large enough to contain many of the elements of volume h^r that correspond to a single quantum state.

(8) *Use of the New Form of Maxwell-Boltzmann Distribution Law.*—The Maxwell-Boltzmann distribution law in its new quantized form, as given by equation (14), may now be used to solve many problems that were very bothersome in pre-quantum theory days.

Since equation (14) gives us the number of molecules of a gas in each given state of energy ε_i, we can obviously calculate the total energy of these molecules and by differentiation with respect to temperature obtain the specific heat.

This as you know has in large measure solved the problem of the changing specific heat of diatomic gases. Thus at low temperatures where all the molecules are in the lowest state of quantized rotation, the specific heat drops to the value $C_v = 3/2\ R$, the same as for monatomic gases, and at higher temperatures as the higher quantized rotational states become excited we gradually approach the classical value $5/2\ R$. Also at still higher temperatures we find that quantized vibrational states begin to come in, raising the specific heat even above $5/2\ R$. The qualitative picture of these changes now seems entirely certain, and in many cases the quantitative application of the theory to actual gases is worked out and found to be satisfactory.

I wish also to call your special attention to the circumstances that nothing in our method of development has limited the application of the Maxwell-Boltzmann distribution law merely to those elements of a system for which we ordinarily use the term "molecules." If we have a system made of other kinds of elements than ordinary molecules, we may still be able to apply the Maxwell-Boltzmann distribution law.

Thus we may regard the transverse and longitudinal modes of

vibration of an elastic solid as the elements of our system and determine the average energy for each kind of mode of vibration present, and hence the total energy and by differentiation the specific heat of the solid. This has led, as you know, in the hands of Debye, to a very satisfactory theory of the specific heat of solids.

We may also treat in the same way the electromagnetic modes of vibration in a hollow cavity, or hohlraum. For the number of modes of vibration per cubic centimetre of frequency ν to $\nu + d\nu$, we easily obtain

$$dN = \frac{8\pi\nu^2}{c^3}\, d\nu \tag{16}$$

and by applying the Maxwell-Boltzmann distribution law to these quantized modes of vibration obtain for their average energy

$$\varepsilon_{\text{av.}} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}. \tag{17}$$

Hence by combination we easily derive the Planck distribution law for black-body radiation

$$d\mu = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1}\, d\nu. \tag{18}$$

The derivation is specially interesting for its simplicity. The quantum theory is applied by allowing only those discrete values for the energy of a mode of vibration permitted by the rules of quantization. It is not applied in the extreme form involving corpuscular radiation.

(9) *Application of Statistical Mechanics to Concentrated Systems.*—Up till now we have been discussing problems which could be treated by using the Maxwell-Boltzmann distribution law, and although there are many other problems in which this law can be used, I think that we have taken enough to give an idea of the importance and scope of the principle. We must now say something about systems which cannot be treated by this method.

If we look again at equation (1) as an expression of the

Maxwell-Boltzmann law, we note that ε is the energy of a molecule when its coördinates and momenta fall in the region $dq_1 \ldots dp_n$. In the case of concentrated systems, however, where the molecules are near enough together to interact continuously with each other, it is evident that the energy of a molecule may depend not only on its own coördinates and momenta, but on those of neighboring molecules as well. Indeed, it may be impossible to separate the energy of the system as a whole completely up into parts belonging to the individual molecules. Sometimes we can perhaps help ourselves out of this difficulty by taking ε as the rate of increase in the energy of the system per molecule added to the region $dq_1 \ldots dp_n$.[5] In general, however, we have to devise new methods for the treatment of concentrated or other systems of molecules where we must take account of the forces that one molecule exerts on another.

An interesting example of the kind of difficulty I have in mind is furnished by solutions of ionized electrolytes. Since the electric force from a charged particle falls off only as the inverse square of the distance, the ions of such solutions, even at high dilutions, exert important forces on their neighbors. And this, as you know, has led to the Milner-Debye theory of interionic attraction to explain the deviations of electrolytes from the laws of a perfect solute.

Another example of the difficulty occurs when we deal with compressed gases in which the forces between the molecules must be considered. In such a case the perfect gas laws will no longer obtain, and the statistical mechanical treatment leads to more complicated equations of state.

To my mind the most important work that has been done in the case of systems that cannot be treated by the simple Maxwell-Boltzmann equation is that of Ehrenfest and Trkal[6] on chemical equilibria in gases. In this investigation the authors can take the atoms themselves as the ultimate elements of the system, and allow them to be dissociated or combined into molecules or condensed into crystals in any desired way. Under these circumstances it would of course be impossible to specify the state of an atom

[5] See TOLMAN, *Jour. Amer. Chem. Soc.*, **44**, 75 (1922).

[6] EHRENFEST and TRKAL, *Proc. Amsterdam Akad.*, **23**, 162 (1920). See also PAULING and TOLMAN, *Jour. Amer. Chem. Soc.*, **47**, 2148 (1925).

solely by giving the values of its own coördinates and momenta without reference to the coördinates and momenta of other atoms.

To treat this problem Ehrenfest and Trkal take the sound and fundamental step of returning to a consideration of a micro-canonical ensemble of systems identical in structure with the one of interest, and then determining the conditions of chemical combination and distribution between solid and vapor which prevail throughout different portions of the phase space. In this way they are able to determine in a most beautiful way the most probable state of chemical combination and of distribution between solid and vapor, and to show that states differing appreciably from this most probable state have only an infinitesimal chance of occurrence.

(10) *The Principle of Dynamical Reversibility.*—So far to-day we have been considering the question of the probable distribution of atoms and molecules in the condition of equilibrium, and have said nothing about the mechanisms by which molecules pass from one state to another. Even in a condition of equilibrium, however, molecules must be continually passing from one state to another so that equilibrium is in the nature of a steady condition, the number of molecules leaving any state per second being equal on the average to the number rearriving from other states.

Of the various principles governing the passage of molecules from one state to another, there is a very interesting one which may be called the *principle of microscopic reversibility*[7] to which I wish to devote the rest of our time to-day. To discuss this principle intelligently, we must first discuss the older *principle of dynamical reversibility.*

The possibility of the "time reversal" of any dynamical motion is a well-known mechanical principle. The proof of this principle, that the reverse of any given motion of a system is also a possible motion of the system, can easily be obtained if we consider the equations of motion in the Lagrangian form:

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = Q_i. \qquad (19)$$

[7] For a partial consideration of the history of this principle see TOLMAN, *Proc. Nat. Acad.*, 11, 436 (1925).

Rewriting these equations so as to show the dependence of the Lagrangian function and the external forces Q_i on the generalized coördinates $q_1 \ldots q_n$ and generalized velocities $\frac{dq_1}{dt} \cdots \frac{dq_n}{dt}$, we obtain

$$\frac{d}{dt}\frac{\partial}{\partial\left\{\frac{dq_i}{dt}\right\}} L\left(\cdots q_i \cdots \frac{dq_i}{dt} \cdots\right) - \frac{\partial}{\partial q_i} L\left(\cdots q_i \cdots \frac{dq_i}{dt} \cdots\right) = Q(\cdots q_i \cdots). \quad (20)$$

Since in general, however, L is quadratic in the velocity terms $\frac{dq_i}{dt}$, equation (19) can obviously be rewritten in the form

$$\frac{d}{d(-t)}\frac{\partial}{\partial\left\{\frac{dq_i}{d(-t)}\right\}} L\left(\cdots q_i \cdots \frac{dq_i}{d(-t)} \cdots\right) - \frac{\partial L}{\partial q_i}\left(\cdots q_i \cdots \frac{dq_i}{d(-t)} \cdots\right) = Q(\cdots q_i \cdots). \quad (21)$$

Hence if

$$q_i = \phi_i(t) \quad (22)$$

is a solution of the equations of motion, it is evident from the identity of the two forms of the equations (20) and (21) that

$$q_i = \phi_i(-t) \quad (23)$$

is also a possible solution. The result means that if at any given instant we reverse the direction of all the velocities of such a dynamical system, it will then retrace its former path, having at each instant on the reverse path the same position and reverse direction of its velocities as at the corresponding time in the original motion.

Limitations to this "principle of reversibility" will obviously arise if the Lagrangian function L or the external forces Q_i should contain terms of the first or other odd degree in the velocities. An interesting example of this occurs in the case of the motion of a charged particle in an external magnetic field.

Here a reversal in the direction of that component of velocity, which is perpendicular to the field, will lead to a reversal in the direction of the force on the particle and thus exclude the possibility of the reverse motion. Thus, as has been pointed out in this connection by Einstein and Ehrenfest, if we consider a Bohr hydrogen atom in an external magnetic field with the electron rotating in a plane perpendicular to the field, the time reversal of this motion will not be possible, since the magnetic force will, for one direction of rotation, be acting towards the nucleus, and for the other direction of rotation away from it. Hence one of the orbits will have a different velocity of rotation than the other. Special attention, however, should be called to the possibility and indeed perhaps propriety of including in the time reversal a reversal in the direction of the electric current which produces the external magnetic field.

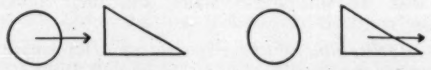
For our present purposes there are two things of interest to note which we may expect to hold, at least in the absence of an external field. In the first place, if we have a molecule in any given state performing external or internal motions, then it will be entirely possible to have another molecule of this same kind performing the reverse of those motions. Or in other words, if i is a possible state of a molecule, then the *reverse* of that state $-i$, which can be obtained from the original state by an instantaneous reversal in the direction of all the components of velocity of its various parts, leaving everything else unchanged, will also be a possible state of the molecule. In the second place, if we consider any interaction or collision between a pair of molecules, presumably including light quanta, in which a pair of molecules go from states i and j to k and l, then a similar collision in which the molecules go from $-k$ and $-l$, to $-i$ and $-j$ will also be possible. Thus introducing Boltzmann's nomenclature, the collisions $\binom{i,\ j}{k,\ l}$ and $\binom{-k,\ -l}{-i,\ -j}$ are both possible.

(11) *The Principle of Microscopic Reversibility.*—These two conclusions immediately lead to the principle of microscopic reversibility. This principle applies to a system of molecules which has come to equilibrium. Referring to the pair of reverse processes just considered, it is evident that in such an equilibrium system the number of molecules leaving the collision $\binom{i,\ j}{k,\ l}$ will

on the average be the same as the number entering the reverse collision $\begin{pmatrix} -k, -l \\ -i, -j \end{pmatrix}$. Or more generally, we may state as the principle of microscopic reversibility the conclusion, or postulate as you prefer, that in a molecular system which has come to equilibrium any elementary molecular process and its reverse occur with equal frequency.

Let me illustrate this principle with the help of these two rather far-fetched models of molecules. One of these, the sphere, might be more or less like an argon atom, and the other, the wedge-shaped one, more like a hydrogen chloride molecule with different properties in different directions. Consider now a collision in which the sphere comes and hits the vertical face of the wedge. Since the two have been made with the same mass, the sphere is brought to rest and its kinetic energy and momentum are acquired by the wedge.

FIG. 1.



Now in accordance with the principle of dynamical reversibility, the reverse of this motion should also be possible. Hence as you see, it is possible to have the reverse collision in which the wedge starts moving *in the direction of its vertical face* and is brought to rest by the sphere. Furthermore, by the principle of microscopic reversibility we must expect in a system which has come to equilibrium to have on the average the same number of the two kinds of collisions.

I wish, however, to call your attention to a specially important feature of the situation. The original collision ends with the wedge moving in the direction of its apex, while the reverse collision starts with the wedge moving in the opposite direction away from its apex. Or in general, the reverse of any original molecular process starts with the molecules in states which are the *reverse* of those in which they have been left by the original process and ends with the molecules in states which are the *reverse* of those in which they entered in the original process. Hence the

principle of microscopic reversibility must *not* be construed, as is sometimes done, at least by implication, to mean an equality between the number of processes of the type $\binom{i,\ j}{k,\ l}$ and those of the type $\binom{k,\ l}{i,\ j}$, but rather an equality with the number of processes of the type $\binom{-k,\ -l}{-i,\ -j}$. Indeed a direct change of the type $\binom{k,\ l}{i,\ j}$ may be impossible, as in the present case, since, as you see, if I start out with the wedge moving in the direction of its apex as it is left at the end of the original collision, no collision would be possible which would bring the wedge to rest, transferring all the momentum and energy to the sphere. This means that in general in a system at equilibrium the constant quota of molecules in any given state must be maintained by a cyclical set of steps, rather than by pairs of inverse steps, provided, of course, that we distinguish states and their reverse from each other.

(12) *Applications of the Principle of Microscopic Reversibility.*—This principle of microscopic reversibility has proved a very useful tool for investigating the rates of molecular processes.

Thus, if I know how often the absorption of radiation by atoms occurs in accordance with the symbolic equation

$$h\nu + A_i \rightarrow A_j \tag{24}$$

where A_i and A_j are two different quantum states of an atom A, then I can conclude that at equilibrium the process

$$A_{-j} \rightarrow A_{-i} + h\nu \tag{25}$$

will occur equally often, where A_{-j} and A_{-i} are the reverse of the previous states. On the other hand, however, from the principle of correspondence, we can assume that in this special case the process given by (25) has the same tendency to occur as

$$A_j \rightarrow A_i + h\nu. \tag{26}$$

Hence, since the Maxwell-Boltzmann distribution law gives us a relation between the numbers of atoms in states i and j present at equilibrium, we can obtain an extremely useful relation between

the *specific* rates of absorption and emission. This was first done by Einstein in his famous 1917 paper, where he used the result to give a derivation of the Planck radiation law quite different from the one we considered a few minutes ago, in that it agrees in spirit with the extreme form of the corpuscular light quantum theory.

The principle of microscopic reversibility can also be used to derive a relation between the probabilities of collisions of the first and second kinds as was first done by Klein and Rosseland. In a collision of the first kind a fast-moving electron gives up its kinetic energy to an atom raising it to a higher quantum state, while the reverse of this process in which a slow-moving electron acquires kinetic energy at the expense of an excited atom constitutes a collision of the second kind. It is very convenient to have a theoretical relation connecting the probabilities of these two kinds of collisions, since usually it is experimentally feasible to measure only the probability of one or the other of the two kinds of collisions. Thus Doctor Glockler, working in the Gates Chemical Laboratory, has found that fast-moving electrons will knock a helium atom from the $1\,S$ to the $2\,s$ state only when they have within a tenth of a volt of the exact kinetic energy necessary for the transition. When they have appreciably more than the kinetic energy necessary for the transition, they quite surprisingly fail to work at all. From this fact it has been possible to conclude that the corresponding collision of the second kind in which the helium atom drops from the $2\,s$ to the $1\,S$ state by giving up its energy to an electron can only occur when the colliding electron is moving so slowly as to remain for a reasonably long time in the neighborhood of the excited atom.

I hope these two examples will illustrate to you the interesting sort of conclusions that can be drawn from the principle of microscopic reversibility. The principle has also been of value in interpreting the rates at which molecules can be chemically activated.[8]

[8] See TOLMAN, *Jour. Amer. Chem. Soc.*, 47, 2652 (1925). At the time of this article the principle of microscopic reversibility had not yet been formulated in its correctly precise form so as to distinguish properly between the *reverse* process $\begin{pmatrix} -k, & -l \\ -i, & -j \end{pmatrix}$ which occurs with the same rate as the *original* process $\begin{pmatrix} i, & j \\ k, & l \end{pmatrix}$ and the *inverse* process $\begin{pmatrix} k, & l \\ i, & j \end{pmatrix}$ which may not be able to occur at all.

I have to thank you again for the kindness and patience with which you have listened, and realize that some of the material may have seemed pretty old stuff to you. I myself am so enthusiastic about the possibilities of statistical mechanics that I am afraid I may make myself something of a bore. In the next lecture we shall consider systems which have not yet come to a condition of equilibrium. This field is really a good deal harder and hence less developed than the one we have been discussing to-day. Perhaps for that very reason, however, it will be easier to present what we do know in a more qualitative and less mathematical form.

THE GLOW TEST FOR METALS OF THE PLATINUM GROUP.

BY

C. W. DAVIS.

Associate Chemist, Rare and Precious Metals Experiment Station (Reno, Nev.), Bureau of Mines, Department of Commerce, in Coöperation with the University of Nevada.

INTRODUCTION.

CURTMAN and ROTHBERG [1] applied the glow reaction to the detection of the metals of the platinum group in 1911 and since that time the method has been used extensively for that purpose. They describe the test as follows:

"The substance to be tested is brought into solution by any of the common methods and about 0.2 c.c. of this solution is absorbed in a piece of thin asbestos paper by alternately dipping the paper into the solution and heating until the required volume has been absorbed. The moist paper held by one end in a pair of tongs is now heated to redness in the Bunsen flame, then removed, and after the redness has ceased, but while the paper is still hot, it is brought into a stream of a mixture of illuminating gas and air from a Bunsen burner. If platinum is present, the asbestos paper will begin to glow."

While experimenting with the glow reaction, using conditions which he had discovered gave it great delicacy, Mr. T. W. Gruetter,[2] Grants Pass, Ore., found that acid solutions of copper concentrates, copper-nickel alloys and of copper salts gave a positive reaction for platinum group metals. After duplicating these tests the author found that a solution containing C. P. copper sulphate, which gave no spectroscopic evidence of the presence of platinum group metals would give the same test if the asbestos was still quite hot when put into the gas stream. Since the glow reaction has frequently been used as an "infallible" confirmatory test for metals of the platinum group, the importance of this discovery and the desirability of further study of the reaction are apparent.

The following subjects are taken up in this paper: The theory

[1] *Jour. Am. Chem. Soc.*, 33, p. 718, 1911.

[2] Private communications, 1925.

of contact catalysis with special reference to the glow reaction; the effect of different factors (developed in the theory) on the glow reaction; and the conditions that should be maintained to give reliable results when the glow reaction is used as a test for the platinum group metals.

ACKNOWLEDGMENT.

It is a pleasure to acknowledge the kind coöperation of Mr. T. W. Gruetter, of Grants Pass, Ore., who not only called attention to the desirability of this investigation, but also assisted in the preparation of this paper by numerous suggestions.

THEORY.

For a better understanding of the glow reaction a brief discussion of the principles upon which it depends will be presented.

Mechanism.—The glow reaction, a case of surface combustion, is a type of contact catalysis which involves the reaction of gases at a solid surface; the surface adsorbs the gases resulting in their activation and accelerated reaction (catalysis). The substance which causes such an effect is called a catalyst and has the same chemical composition after such a reaction as it had previous to it. The gaseous adsorption by the catalyst is usually defined as the tendency of the solid to condense upon its surface a layer of any gas that may be present and is determined by the relative length of time that the gases impinging on the solid surface are held before evaporating.

Although adsorption is doubtless essential to catalytic activity, the amount of adsorption cannot be taken as a measure of the activation. Bancroft[3] has explained this as follows: "The adsorption of some of the reacting substances or of the reaction products may be so great as to interfere with the free flow of matter to and from the surface of the catalyst, or it may be that the activation is greater at higher temperatures or—which is certainly a factor—that the rate of reaction of the activated gases is very much greater at higher temperatures. We should, then, have adsorption decreasing with rising temperature, activation varying in an unknown way with the temperature, and the rate of reaction of the activated gases increasing rapidly with rise of temperature."

[3] Bogue, "Colloidal Behavior," p. 264, 1924.

What takes place in activation is not definitely known, but a great deal of speculation, based on experimental evidence, has been made concerning it. Some gaseous catalyses undoubtedly take place through the formation of definite chemical compounds of the adsorbed and adsorbing substances with more or less rapid alternation or reversal of the reactions involved while other cases are thought to occur through the formation of temporary, intermediate, indefinite compounds.[4]

The mechanisms of these actions have been variously thought of as involving bombardment of adsorbed molecules or atoms; the number, orientation and spacing of which (at the surface of the catalyst) being important in determining the effectivity of the bombardment and the consequent increased reactivity. The making or breaking of bonds between the adsorbed substance and the catalyst has been pointed out as a possible explanation of temporarily activated radicles, and the accumulation and expulsion of electric charges has been considered to have some effect.[5]

Application to the Glow Reaction.—Four operations are involved in using the glow reaction as a test for the platinum group metals:

(1) The preparation of the solution to be tested;
(2) The absorption of this solution by a support;
(3) The heating of this impregnated support; and
(4) The placing of this heated support in a combustible gas (the actual glow reaction).

The first three operations constitute the preparation of the catalyst which is to be used to accelerate the reaction between a combustible gas and oxygen. The properties of this catalyst which are of importance in this connection are its structure, its inherent characteristics, and the effect of poisons.

Structure of the Catalyst.—Adsorption is dependent on the area and configuration of surface and for most practical uses depends on a porous structure.[6] Anything that reduces the

[4] For specific examples see: Engler and Wohler, *Zeit. Anorg. Chem.*, **29**, 1909; Lamb, Bray and Frazier, *J. Ind. Eng. Chem.*, **12**, p. 217, 1920; Taylor, "Treatise on Physical Chemistry," p. 989, 1925; Larson and Smith, *J. Am. Chem. Soc.*, **47**, p. 354, 1925.

[5] For articles on mechanism of contact catalysis see: Bogue, work cited, p. 259; Langmuir, *J. Am. Chem. Soc.*, **37**, p. 1139, 1915, **38**, pp. 1145, 2221, 1916, **39**, p. 1848, 1917; Taylor, work cited, p. 988.

[6] Briggs, *Proc. Roy. Soc.*, **100A**, p. 97, 1921; Armstrong and Hilditch, *Proc. Roy. Soc.*, **99A**, p. 490, 1921; Bancroft, work cited, p. 265.

effective area of the surface reduces adsorption. Such a reduction of area is produced by sintering or by the action of protective coatings or "poisons." Sintering, on heating, has been prevented to a large extent by fastening the catalyst to a rigid support. In the case of nickel, it was found that when supported by diatomite brick it could be heated to 500° without detriment, but that when unsupported in this way its catalytic effect was destroyed at this temperature.[7] Platinized asbestos can catalyze the oxidation of carbon monoxide after heating at high temperature, but platinum black changes very much at 300°.[8] In this connection Bancroft[9] has pointed out that although sintering is favored by the high temperatures of exothermal reactions, the reaction itself tends to break up the mass and may increase its catalytic activity.

A phenomenon known as "promoter action" is related to the structure of the catalyst. It is well known that the activity of certain catalysts for certain reactions can be greatly increased by the addition of a small quantity of another substance and in some cases a mixture of several catalysts has been found more active than any one of them.[10] Enhanced activity at a solid-solid interface is quite common,[11] and this may explain part of the promoter effect, but Bancroft[12] considers this not the important factor and suggests that a possible explanation is that the promoter prevents sintering or melting, or that one catalyzer may activate one reacting substance and the promoter be more effective in activating another, and Larsen and Smith[13] suggest that a promoter may decrease the stability of reaction products or poisons and thus activate the catalyst.

The structure usually considered to give the best catalyst has a large surface, a condition which is satisfied by a state of fine division. This result, in the case of the glow test, is obtained by heating the impregnated support, to dry and decompose its

[7] Taylor and Gauger, *J. Am. Chem. Soc.*, **45**, p. 920, 1923; Armstrong and Hilditch, work cited; Kelber, *Ber.*, **49**, p. 55, 1868, 1916.

[8] Pollard, *J. Phys. Chem.*, **27**, p. 366, 1923.

[9] Bogue, work cited, p. 274.

[10] Rideal and Taylor, "Catalysis in Theory and Practice," p. 31, 1919; Pease and Taylor, *Jour. Phys. Chem.*, **24**, p. 241, 1920; Bancroft, "Applied Colloid Chemistry," p. 56, 1921; Ipatiew, *Ber.*, **43**, p. 3387, 1910.

[11] Taylor, "A Treatise on Physical Chemistry," pp. 963, 982, 1924.

[12] Bogue, work cited, p. 263.

[13] Work cited, p. 354.

absorbed salts. The amount and concentration of the solution absorbed and the area of the surface of its support should have an effect on the catalyst produced.

That the rate of drying of the adsorbed salts may have some effect on the catalyst used in an oxidizing gas reaction is shown by Lamb, Bray and Frazier,[14] who state that slow drying gives the most active catalyst for the oxidation of carbon monoxide.

To sum up: The factors which may influence the nature of the glow reaction catalyst by their effect on its structure are the size, thickness and porosity of the asbestos, the concentration and amount of the solution being tested, the rate of drying, the temperature and time of heating, the presence of poisons or promoters, and the presence of substances in solution which might change it; as for example, Curtman and Rothberg found that strong nitric acid caused the asbestos to swell up and that some salts left heavy residues on ignition.

Inherent Character of the Catalyst.—The activity of the catalyst that is dependent on its inherent nature is determined by the substances dissolved in the solution under test and their subsequent reactions on heating. Platinum, palladium, iridium and rhodium are known to be active catalysts in promoting oxidizing gaseous reactions and to give the glow test. Other substances adsorb gases readily and have been said to be more or less effective in catalyzing gaseous oxidation when properly prepared. Such material therefore might be expected to give the glow reaction. This catalytic effect is independent of the property which all incandescent substances possess to about the same degree, that of accelerating gaseous combustion.[15] Whether the catalyst will be present as an oxide or in the metallic condition will in most cases be determined by whether it is heated in an oxidizing or reducing atmosphere, except for the metals not easily oxidized and the oxides not easily reduced.

Some of these catalysts are known to have a specific effect. For example, in the presence of certain oxides, carbon monoxide

[14] Work cited.

[15] Bancroft, "Applied Colloid Chemistry," pp. 49–63. Lamb, Bray, Frazier, *Jour. Ind. Eng. Chem.*, **12**, p. 213, 1920. Bosch, Mittasch, Beck, U. S. Pat. 1,211,394. Bone, *Phil. Trans.*, **206A**, p. 1, 1906; JOUR. FRANK. INST., **173**, p. 101, 1912. Meunier, *Compt. Rend.*, **152**, p. 194, 1910. Sabatier, Maihle, *Compt. Rend.*, **147**, p. 16, 1908. Rideal and Taylor, "Catalysis in Theory and Practice," p. 31, 1919.

can be oxidized preferentially by gaseous oxygen even when hydrogen makes up 99 per cent. of the gas mixture.[16] Benton [17] has shown that carbon monoxide is adsorbed more than hydrogen so that at the surface of the catalyst the former would predominate and consequently react preferentially. There are other specific catalytic activities, however, that do not follow this reasoning. As pointed out by Taylor [18] of several metals, all of which adsorb carbon monoxide and hydrogen markedly, some catalyze a reaction between these gases while others are quite inactive. Other similar cases have been noted. Taylor (work cited, p. 293) thinks this specificity of adsorption and catalytic activity may be due to "the disturbance exercised by the process of adsorption on the configuration of the adsorbed molecule," and to the orientation of the adsorbed molecule and the actual distances between the surface atoms of the catalyst. At higher temperatures the specificity is less and at incandescence is absent, because the reaction will take place so readily in the gas phase.[19]

Effect of Poisons.—The so-called poisoning of catalysts is considered to be due to the adsorption of substances (gas, liquid or solid) which, as shown by Taylor,[20] decreases the rate at which the reacting substances reach the catalytic surface, or, as pointed out by Bancroft,[21] which prevents them from reaching it, and thus decreases the reaction velocity or the catalytic action. The effect may be produced by the initial adsorption of gases or by the formation of reaction products. There are a vast number of examples of both types.[22]

Because certain gases prevent the combustion of hydrogen in the presence of finely divided platinum and these same gases prevent hydrogen from burning in oxygen under the influence of an electric spark, Moureau and Dufraisse [23] reject the previous interpretations and consider that poisons decompose the peroxides

[16] Rideal, *J. Chem. Soc.*, 115, p. 993, 1919.

[17] *J. Am. Chem. Soc.*, 45, p. 887, 900, 1923.

[18] "Treatise on Physical Chemistry," p. 990, 1924; Bogue, "Colloidal Behavior," p. 297, 1924.

[19] Bone-Bancroft, "Applied Chemistry," pp. 47, 62, 1920.

[20] *Trans. Am. Electro Chem. Soc.*, 36, p. 149, 1919.

[21] Work cited, p. 267.

[22] Bogue, work cited, pp. 267–270.

[23] *J. Chem. Soc.*, 127, p. 1, 1925.

which result from the union of oxygen and the catalyst, or in the case of the spark, the oxide of hydrogen is decomposed by the poison.

Since minute amounts of many substances are known to destroy the activity of catalysts [24] used for oxidation reactions, the presence of such "poisons" in the solution to be tested would be expected to decrease the sensitivity of or destroy the power of the catalyst which causes the glow reaction. But Curtman and Rothberg [25] found that under the conditions of their tests relatively large amounts of such substances in the solution had little or no detrimental effect. It would seem, therefore, that the effect cannot be considered as a case of poisoning but rather as a case of reaction with or mechanical interference with the catalytic surface where those substances which leave a heavy residue on the asbestos paper on ignition impair the sensitivity of the test.

The constituents of the gas used in heating the impregnated asbestos may have some effect on the catalyst. A catalyst may become poisoned by heating in the presence of various substances so that the presence of such impurities in the gas used for heating the impregnated asbestos might be detrimental. Some of these poisons may have no effect on the glow reaction under the conditions used; as for example Curtman and Rothberg [26] noted that if the catalyst used in the glow reaction was heated repeatedly it finally lost its ability to glow, but the effect was too slow to be detrimental to the test. This action was probably caused either by a "poison" in the gas or by sintering of the catalyst. The specificity of adsorption is again important in this connection since it has been shown that while carbon monoxide adsorbed by platinum is not easily removed, when adsorbed by palladium it is easily displaced by hydrogen.[27]

The Actual Glow Reaction.—The fourth operation performed in making the glow test takes place when the catalyst, prepared as explained previously, while still hot (but not incandescent),

[24] Maxted, *Jour. Chem. Soc.*, **115**, p. 1050, 1919; **117**, p. 501, 1920; **119**, pp. 225 and 1286, 1921; **121**, p. 1760, 1922; **127**, p. 73, 1925. Trotman, Chapman, Ransbottom and Trotman, *Proc. Roy. Soc. London*, **107A**, p. 92, 1925.

[25] Work cited, p. 722.

[26] Work cited.

[27] Taylor and Burns, *J. Am. Chem. Soc.*, **42**, p. 1285, 1921.

is placed in a combustible gas. The gases are adsorbed by the catalyst and react at its surface. The heat of adsorption and the heat of reaction raise the temperature until incandescence is produced at the surface. The incandescence, the glow reaction, seems to be an example of surface combustion, where the rate of combustion is so accelerated that the gas particles react immediately on reaching the catalyst. As the catalyst absorbs more heat it will eventually become hot enough to ignite the gas which will then burn at the orifice, unless heat is removed from the catalyst. In the glow test the gas is cold in comparison with the hot catalyst and will therefore remove some heat. Another important factor is the size of the hot body; it is well known that while a large hot body may ignite a gaseous mixture at temperatures around 600° C. a hot platinum wire under certain conditions may be melted in the same mixture without igniting the gases. This seems to be due to the lag (the time required for a heated body to ignite a gaseous mixture) which may be as great as several seconds for small heated bodies. The results of experiments have led to the conclusion that " for ignition by a hot wire, such a temperature must necessarily be reached that the difference between the time lags for various mixtures is negligibly small." [28]

The presence of " poisons " in the gas used for this final part of the test may decrease the activity of the catalyst. The composition of the gas used should also be considered since, as previously stated, one catalyst may be the most efficient in oxidizing a certain gas, while another catalyst may have its greatest effect on some other gas, as, for example, the preferential oxidation of either hydrogen or carbon monoxide can be produced by the use of a suitable catalyst.[29] Other factors which may influence the glow reaction are: The temperature of the catalyst when it is placed in the gas stream, the temperature of the gas and the rate of flow of the gas.

EXPERIMENTAL PART.

The preceding discussion has brought out those factors which seem to control the glow reaction. They are: With regard to the support, the quantity of solution absorbed on a given area, its inertness toward reactions with the test solution, its inertness on heating, its structure and its size; with regard to heating the

[28] Naylor and Wheeler, Safety of Mines Research Board, Paper No. 9.
[29] Rideal, work cited.

impregnated support, the rate of drying, the time and temperature of heating, the source of heat (if gas is used, its composition and poison contents); with regard to placing the heated catalyst in the gas stream; the temperature of the catalyst and the temperature, composition and rate of flow of the gas, and with regard to the solution to be tested; its content of possible catalytic material (its nature and concentration), its content that may act as a poison, and its content that might effect the structure of the absorbent or of the catalyst.

The Support.—The kind and size of the catalyst support has been studied.[30] Asbestos paper has been found to be very satisfactory and the smaller the portion used to absorb the solution the more delicate is the test; Gruetter having obtained the glow reaction with 0.00005 mg. of platinum by using an asbestos thread and hot gas. The practical limit is determined by a size which is strong enough to support itself under the conditions of the test and for the experiments which follow asbestos paper 0.3 mm. thick, cut into strips about 3/32 inch wide and 1½ inches long were used. One end of each strip was ignited to burn organic matter and about ½ inch of this end was used to absorb the solution being tested.

Heating the Catalyst. (Temperatures at which they are formed.)—No noticeable difference in the activity of catalysts of the platinum metals was observed when the absorbed solutions were dried at different rates, but in order that reproducible conditions be used the impregnated strips were dried at 105° C.

To eliminate the effect of various possible detrimental substances that might be present in the heating gas and to secure better control, all heating was performed on an electrically heated plate, in air.

It is evident that there is a temperature below which an active catalyst cannot be formed, and it is well known that heating for a long time at high temperatures will destroy the activity of catalysts.

Curtman and Rothberg[31] found that under the conditions of their tests solutions of ruthenium or osmium failed to give the glow reaction and suggested that this was caused by the

[30] Curtman and Rothberg, and Gruetter, work cited.
[31] Work cited.

volatilization of these elements. Their explanation was substantiated and a glow obtained when certain conditions were maintained. A series of tests showed: That if the catalyst was prepared by heating the dried, impregnated, asbestos at 165° C. for two or three minutes (thirty minutes did no harm) and was immersed in a gas stream heated to 350°–450° C. for a few seconds, the catalyst became incandescent. Chloride solutions of all the other platinum group metals gave the glow under these conditions as did also solutions of copper nitrate and copper chloride. Copper sulphate solution gave an active catalyst, however, only when the impregnated asbestos was heated to about 660° C. (heating at 700° gave a more active catalyst), indicating that the catalyst in this case was copper oxide, since Hofman and Wanjukow [32] give 653° as the temperature at which copper sulphate heated in air starts to change to the oxide.

Other tests showed that although the catalytic effect of osmium was destroyed by heating for about a minute at 400° C., this treatment had certain advantages in the preparation of catalysts from the other platinum group metals, as will be explained later.

Since they have been shown to have some significance, the temperatures 165°, 400°, and 700° C. will be used for preparing the catalyst in most of the tests which follow.

Temperature of the Gas and the Catalyst.—It has been shown that the temperature has an important effect on the rate of the reaction of gases and on the activity of a catalyst. In the glow reaction the gases and the catalyst are in contact, so that the regulation of the temperature of either one will control the rate of reaction at the start. Methods that have been used for the glow test put the catalyst, heated to an unknown temperature, into a cold gas stream or, to increase the delicacy of the test, into a heated gas stream. As it would be very difficult to maintain the strip of catalyst at any definite temperature, it was decided to regulate the temperature of the gas stream which, in turn, would heat the cold catalyst and regulate its temperature at the start of the reaction. To produce this heating effect the gas must come through an orifice of sufficient size so that an adequate supply of heated gas will reach the catalyst.

[32] *Met. and Chem. Eng.*, 10, p. 172, 1912.

In combustion a definite ratio of air to gas will be catalyzed most readily and this ratio may vary when different gases are involved. The necessity of determining this optimum ratio for the glow reaction gases may be eliminated by using a small jet of combustible gas spurting into the air. This will give all possible ratios of air and gas at some points in the mixture. The point at which this optimum condition exists was determined by immersing an active catalyst in the stream and noting the positions at which it glowed. A portion at the centre of the emerging stream, rich in gas, gave no reaction, but it was surrounded by an envelope in which the catalyst glowed. To prevent the possibility of placing an active catalyst wholly within the "dead" space, the gas stream should not be too large.

A tube having an orifice of ⅛ inch in diameter was chosen for our experiments, since this gave sufficient gas to heat the catalyst but did not produce an excessive "dead" space.

The rate of flow of the gas is important in its conduction of heat, since its effect will be one of heating at the start and of cooling when the catalyst becomes hotter than the gas. To standardize conditions a flow was used such that, when lighted, a flame 1½ inches long was produced.

In our experiments the tube through which the gas passed was heated and the approximate temperature of the emerging gas was determined by placing a precious metal thermocouple junction in it, at a point about ¼ inch from the orifice of the tube, the position at which the catalyst was held in all tests. (The temperatures observed were probably in error because of the uncertainty of the position, the unknown catalytic effect of the thermocouple and the known difficulty of measuring the temperature of a gas stream with a thermocouple of finite dimensions.)

To determine whether the minimum temperature of the gas at which various catalysts (starting at room temperature) would become heated to incandescence might be used as a means of differentiation, a series of tests was made. The results, in the vicinity of the critical points, using two gases, are given in Table I. All catalysts were prepared by heating the impregnated asbestos strip at 165° C. for five minutes and fairly strong solutions of the compounds listed were used.

These results indicate that there is some difference between

the critical points of the different substances; that these points are, as a rule, lower for hydrogen than for illuminating gas; and that the point for copper sulphate is sufficiently high as to differentiate it from solutions of the platinum group metals.

Experiments showed that high gas temperatures gave greater delicacy and shortened the time required for the catalyst to become heated to incandescence, the lag near the critical points being several seconds. At too high a temperature, however, the gas became ignited readily and the osmium and ruthenium did not

TABLE I.
Minimum Temperature of Glow Reaction for Certain Conditions.

Solution of	Highest Temperature at Which No Glow Was Observed. °C.		Lowest Temperature at Which Glow Was Observed. °C.	
	Ill. Gas.	Hydrogen.	Ill. Gas.	Hydrogen.
H_2 Pt Cl_6	160	....	175	25
Pd Cl_2	230	30	250	50
Na_2Ir Cl_6	255	260	275	280
Na_3Rh Cl_6	255	230	275	250
Na_2Ru Cl_5	255	250	275	275
Na_2Os Cl_6	285	230	300	250
Cu NO_3	275	220	290	230
Cu Cl_2	300	280	325	300
Cu SO_4	500	500	....	....

glow. Four hundred degrees C. was found to be satisfactory and was used in all subsequent tests.

Kind of Gas.—The importance of the constituents of the gas used for the glow test, especially at low temperatures, due to the specificity of different catalysts for different gases, has been discussed previously. The gases which may be readily obtained for this test are hydrogen and various types of illuminating gases. Mr. Gruetter suggests the use of fumes from the hot wick of a lamp burning alcohol and ether (after the flame which has been used to heat the catalyst has been extinguished) as a suitable gas. In all of the important tests in this investigation hydrogen, prepared by the action of hydrochloric acid on arsenic-free zinc (washed by passing through water and dried by passage through sulphuric acid), and illuminating gas from the city mains were used. A typical analysis of the latter gas, made at the time the experiments were being conducted, follows:[33]

[33] This analysis and information were kindly furnished by Mr. J. T. Sullivan, Gas and Water Superintendent of the Truckee River Power Company.

Illuminants	2.1% (by volume)
CO	4.7% (by volume)
CH_4	27.9% (by volume)
H_2	62.6% (by volume)
CO_2	0.7% (by volume)
O_2	0.5% (by volume)
N_2	1.5% (by volume)

"The illuminants are principally ethylene and there is a small amount of ethane included with the methane. The gas is absolutely free of hydrogen sulphide but contains 7 to 10 grains of total sulphur per 100 cubic feet, which is principally carbon disulphide."

Several substances which may be present in illuminating gas or impure hydrogen have been known to poison oxidation catalysts and therefore should have some effect on the glow reaction. Each of these gases was mixed with hydrogen and with illuminating gas, the catalysts being prepared by heating the impregnated asbestos at 165° and used cold, and the gas being heated to 400° C. Hydrogen sulphide, about 1 per cent. (by volume), had no apparent effect on the glow obtained by dilute solutions of the metals of the platinum group, but when 5 per cent. was present no glow was given by catalysts made from weak solutions, though catalysts from strong solutions were active. The further addition of the sulphide up to 30 per cent. produced no noticeable change. Carbon dioxide up to 20 per cent. did not decrease the delicacy of the glow reaction but carbon monoxide, about 30 per cent., sulphur dioxide about 1 per cent., or water vapor (introduced by passing the gas through water before heating) prevented the glow of catalysts that contained nearly the limiting quantity of platinum metal that would glow in the absence of poisons. When either hydrogen or illuminating gas was passed through carbon disulphide before heating, the poison effect was very marked, strong solutions of all the platinum metals failing to glow under the conditions of the test. Arsine (produced through the reaction of arsenious oxide, acid and zinc) was an equally poisonous substance, but stibine produced in a similar way, although it decreased the delicacy of the test, did not prevent the glow of catalysts made from strong solutions.

The importance of the presence of "poisons" in gases used for the glow test is thus apparent.

Limit of the Glow Test.—Since pure solutions containing platinum group metals can be concentrated by evaporation before absorption on asbestos, the quantity of metal and not its concentration is the limiting factor for the glow test. The optimum conditions for greatest delicacy are apparently solutions of pure chlorides, very small asbestos strips, hot catalysts, and a hot gas free from poisons. Using a hot gas and a hot catalyst, prepared by absorbing a solution of platinic chloride on an asbestos thread, Gruetter obtained a glow from 0.00005 mg. of platinum. Curtman and Rothberg,[34] using larger absorbents, found the following limits: Platinum—0.002 mg.; palladium—0.0005 mg.; rhodium—0.0009 mg.; and iridium—0.005 mg. Sodium salts were present in the last test, which probably decreased its sensitivity.

In my experiments four series of tests were made, using asbestos strips on a portion of which (3/32 inch by 0.3 mm. by ½ inch) 0.015 c.c. of the chloride solution was absorbed. These strips were dried at 105° C. and all except those containing ruthenium or osmium were heated one minute at 400° C., the exceptions being heated five minutes at 165° C. The first series were introduced while cold into a stream of hydrogen heated to 400° C. Strips containing the following amounts of metal gave the glow test: Platinum—0.00065; palladium—0.00013 mg.; iridium—0.001 mg.; rhodium—0.0006 mg.; ruthenium—0.0006 mg.; and osmium—0.002 mg. The second series was the same, except that illuminating gas was used instead of hydrogen, and the results did not differ appreciably from those of the first. In the third series hot catalysis (about 450° C.) and hot hydrogen resulted in the following limits: Platinum—0.00033 mg.; palladium—0.00006 mg.; iridium—0.0006 mg.; and rhodium—0.0003 mg. In the fourth series the substitution of illuminating gas for hydrogen had no apparent effect.

It is possible that some substances may act as promoters and increase the sensitivity of the glow test and in fact the asbestos may be effective in this way; however, tests showed that bismuth and other suggested promoters interfered with the activity of the catalyst when prepared under the conditions outlined.

Nature of Solutions.—Since copper has been found to give the glow reaction the effects of other oxidation catalysts deserve

[34] Work cited.

investigation, and although it is impossible to make an exhaustive study of all such substances (since it is well-known that various mixtures of inert substances may form catalysts that activate gaseous oxidation), an examination of known oxidation catalysts should help to determine the reliability of the glow reaction as an indicator of platinum group metals.

In these tests both hydrogen and illuminating gas were used at a temperature of 400° C., their flow being regulated as explained previously. The asbestos strips were ignited, impregnated with the solution to be examined and dried at 105° C. One series was heated at 165° C. for three minutes, another was heated at 400° C. for one minute and a third was heated at 700° C. for one-half minute. In these three series the catalyst was cooled to room temperature before immersing in the hot gas. A fourth method (that most sensitive for platinum, palladium, iridium and rhodium) was also used. The catalyst was heated in a Bunsen flame, and, after letting the incandescence die out but while still hot, it was placed in the hot gas stream.

The usual methods of dissolving the platinum metals results in the formation of their chlorides or double chlorides, often in the presence of nitric acid, the latter being removed by repeated evaporation with hydrochloric acid. As will be shown later, it is of advantage to convert certain chlorides to sulphates before using the glow test. The scope of these tests therefore is limited to the study of solutions of chlorides, sulphates and nitrates. Solutions or suspensions of the chlorides and sulphates of the following elements were used: Ni, Co, Fe, Mn, Cr, Cu, Au, Ag, Hg, Bi, Mg, U, V, Mo, Th, Ce, and Zr, as well as nitrates of Ag and Cu; also solutions containing mixtures of chlorides and mixtures of sulphates of: Th and Ce (ratio Th to Ce, 99 to 1), Cu and Co (ratio 3 to 2), Mn and Cu (3 to 2), Cu, Co and Mn (equal parts), Co, Ni and Mn (equal parts); mixtures of nitrates and mixtures of sulphates of: Cu and Ag (99 to 1), Ag and Mn (2 to 1), Ag and Na (equal parts), Cr and Hg (equal parts), Ag, Mn and Co (equal parts), Mn, Cu, Co and Ag (10 to 6 to 3 to 1).

The results of these tests, summarized in Table II, show that: (1) Of all the solutions tested only those containing copper, or silver, or concentrated solutions of cobalt or nickel gave the glow

reaction under the conditions used. (2) Catalysts prepared from strong solutions of silver nitrate, by heating impregnated asbestos at 165° C. are inert but become active after heating at 400° C. (3) Asbestos impregnated with solutions of copper nitrate, copper chloride, cobalt chloride, or solutions of these substances containing small amounts of others becomes a catalyst on heating at 165° C. (4) Catalysts prepared from solutions of copper

TABLE II.

Compounds Giving the Glow Reaction under Different Conditions.

Solutions.	Illuminating Gas.				Hydrogen.			
	Cold Catalyst.			Hot Catalyst.	Cold Catalyst.			Hot Catalyst.
	165° C.	400° C.	700° C.*		165° C.	400° C.	700° C.	
$Cu(NO_3)_2$	Glow	Glow	Glow	Glow	Glow	Glow	Glow	Glow
$Cu\ Cl_2$	"	"	"	"	"	"	"	"
$Cu\ SO_4$	Inert	Inert	"	"	Inert	Inert	"	"
$AgNO_3$	"	Glow	"	"	"	Glow	"	"
Ag_2SO_4	"	Inert	"	"	"	Inert	"	"
$AgCl$	"	"	"	"	"	"	"	"
$CoCl_2$	Glow	Glow	"	"	Glow	Glow	"	"
$CoSO_4$	Inert	Inert	Inert	"	Inert	Inert	Inert	"
$NiCl_2$	"	"	Glow	"	"	"	Glow	"
$NiSO_4$	"	"	Inert	"	"	"	Inert	"
Solutions containing salts of one or more of the following: Cu, Co, Ni, and Ag.	"	"	.....	"	"	"	.....	"
All other salts tested	"	"	Inert	Inert	"	"	Inert	Inert

* Temperatures at which the catalysts were prepared.

sulphate, silver sulphate, nickel chloride, or suspensions of silver chloride become active only by heating the impregnated asbestos to about 700° C. or higher. (5) Catalysts prepared from solutions containing cobalt sulphate, or nickel sulphate become active only by heating at temperatures somewhat above 700° C. (Nickel sulphate starts to decompose at about 702° C. and cobalt sulphate at about 720° C.)

The positive reaction of silver is not serious since the silver can be readily precipitated as the chloride and removed by filtration. The presence of copper, cobalt or nickel, however, is not so easy to remedy, their separation being rather intricate. Cop-

per may be removed from the platinum group metals by precipitation as the thiocyanate as explained by Swanger and Wichers [35] and copper, cobalt and nickel may be separated by methods of fire assay, the former introduces sodium salts, which are detrimental, and fails to remove nickel and cobalt, and the latter, which is undoubtedly the best method that we have for the other platinum group metals, causes a loss of considerable osmium and ruthenium and may result in the loss of some iridium. Other methods of separation have their weak points.

Previous experiments have shown that the regulation of the gas temperature did not give an effective differentiation of copper chloride from the platinum metals by the glow test, but that conversion of the copper to the sulphate gave some promise. This suggested experiments which showed that chloride solutions of Cu, Pt, Pd, Ir, Rh, or Ru, evaporated to fumes with sulphuric acid and diluted, gave solutions that formed active catalysts when heated at certain temperatures; Ru at 165°; Pt, Pd, Ir and Rh at temperatures between 165° and 600° C., and Cu only at temperatures above 660°. Osmium gave no glow under these conditions, but it was found that if the impregnated asbestos heated at 165° C. was cooled, placed in a watch glass and washed by gentle agitation with several changes of distilled water, followed by drying at 165° C., an active catalyst was produced. Further tests showed that the presence of copper in the sulphate treatment of the platinum metal solutions decreased the delicacy of the glow test, but that this could be remedied by washing the catalyst in distilled water. For this treatment, the catalyst of Pt, Pd, Ir, or Rh is best prepared by heating at 400° C.

The sulphates of cobalt and nickel acted in a similar way to copper sulphate.

Although Curtman and Rothberg [36] found that very few substances interfered with the glow test under their conditions, a study of those substances which are known to poison oxidation catalysts was made to determine their effect on the reaction when the catalyst was prepared by heating it at more moderate temperatures. The following substances were used: Solutions of chlorides and sulphates of As, Sb, Au, Ni, Co, Fe, Hg, Bi, Pb, Zn,

[35] *J. Am. Chem. Soc.*, 46, p. 1814, 1924.

[36] Work cited.

Na, K, Li, and grease, in which the ratio of "poison" to platinum metal was about 1000 to 1 (or as great as the solubility of the salt would permit in some cases). Two temperatures were used in preparing catalysts, 165° C. and 400° C., and the gas was used at 400° C. Ni, Co, Fe, Hg and Zn had no noticeable effect on the delicacy of the glow test under these conditions. Grease, an active poison when cold gas was used, was soon removed and the activity of the catalyst restored when the impregnated strip was heated at 400° either on the hot plate or in the hot gas stream. Lead, although it acted as a strong poison, was effectively removed when the solution was fumed with sulphuric acid. Strong solutions of gold chloride were detrimental, but sufficient metallic gold was removed by fuming with sulphuric acid so that the resulting solution gave a satisfactory glow reaction. The alkali metal salts which formed incrustations and decreased the delicacy of the test were quite readily removed by washing the impregnated asbestos strip that had been prepared by heating at 400° C. (as explained for the removal of copper salts), and the catalyst made active. Arsenic, antimony and bismuth were all very detrimental to the test; when present as the chlorides, washing of the impregnated asbestos (after heating) did no good; but when present as the sulphates, they could be removed by washing, so that the asbestos became an active catalyst.

Other tests showed that although the solutions (formed by dissolving the residues produced when platinum metals were mixed with excess sodium chloride and heated in chlorine) would not give the glow test when very dilute, catalysts made from them could be activated by washing with water.

Modified Procedure for the Glow Reaction.—Curtman and Rothberg's method may be applied safely only in the absence of copper, cobalt, nickel and silver; as, for example, when used for a confirmation of platinum metals that have been separated, or in testing an assay bead (carefully prepared so as to be free from copper or nickel) that has been dissolved and the silver removed. It does not include osmium and ruthenium.

Although a separation of the platinum group metals is beyond the scope of this paper, the results of the foregoing experiments indicate that a procedure can be given such that copper, cobalt, nickel and silver will not give the glow reaction, the metals of the

platinum group will give the test, and the detrimental effects of foreign salts will be largely eliminated.

To apply the test the platinum metals must be in solution and to effect this the following procedures may be used. The finely pulverized substance to be tested (sometimes a preliminary fusion with zinc followed by treatment with dilute hydrochloric acid is desirable to effect this) is heated with several portions of aqua regia which, in most cases, will dissolve platinum and palladium and small amounts of the other platinum metals. The platinum metals not dissolved by this treatment (in case it is suspected that some osmium or ruthenium have been dissolved by the treatment with aqua regia a fresh sample should be used) are converted to double chlorides, soluble in water, by mixing the pulverized substance with an excess of sodium chloride, placing in a combustion tube and heating to about 450° C. while passing dry chlorine through the tube. Two special cases are worthy of note: (1) If an alloy containing platinum group metals is present, which consists mainly of silver and gold, with the ratio of silver to gold about 2 to 1 (or greater), the alloy must be treated with nitric acid to remove silver before the treatment with aqua regia, otherwise a coating of silver chloride will be formed which prevents all but a superficial attack by aqua regia. (2) If the alloy has a ratio of silver to gold much less than 2 to 1, its silver will not be dissolved by nitric acid, neither will its gold be dissolved by aqua regia; to effect its decomposition the alloy should be melted with the addition of pure silver and then treated with nitric acid followed by treatment with aqua regia, the two solutions being mixed and the silver chloride removed by filtration. If the precipitate is pink it should be dissolved in an ammonium hydroxide solution and reprecipitated by adding hydrochloric acid. The filtrate, containing palladium that was occluded by the silver chloride, is added to the main solution. Another method of dissolving the alloy of case 2 is to treat alternately with aqua regia and ammonia until all the metal has been dissolved, the ammonia extractions being discarded.

The aqua regia solution which may contain the platinum and palladium is treated separately from the aqueous solution of the double chlorides of the other platinum group metals. The former is evaporated to dryness, at not over 135° C., three or four times

with the addition of hydrochloric acid after each evaporation, to remove nitric acid. (The temperature should be kept down, otherwise platinum or palladium would be rendered insoluble.) The final residue is moistened with hydrochloric acid and diluted somewhat, the insoluble matter being removed by filtration if desired. A few drops of sulphuric acid, sufficient to convert all copper, cobalt, nickel and lead to sulphates, are added and, after evaporating at about 150° C. to fumes to convert soluble salts to sulphates, a little water is added. After settling, the supernatent liquid may be used for the glow test or the precipitate may be removed by filtration and the filtrate, concentrated by evaporation, used. An asbestos strip, ignited to remove organic matter, is soaked in the solution, dried at 105° C., heated at 400° C. for about a minute, and then is held in a gas stream heated at 400° C. for a few seconds. A glow shows the presence of platinum group metals. In the presence of interfering salts the catalyst is then washed by gentle agitation in a watch glass with three or four portions of distilled water. (The washing must be gently done or the asbestos will not hold together.) After heating again at 400° C. for about a minute the catalyst is again held in the gas stream. Osmium or ruthenium would not give the test under these conditions but these elements will be found in the aqueous solutions, as explained previously.

The aqueous solution of the double sodium chlorides of the platinum metals is evaporated at 150° C. after the addition of a few drops of sulphuric acid. It is then ready for the glow test. The asbestos strip impregnated with this solution is dried at 105° C., heated at 165° C. (preferably in a reducing gas), washed with water, heated again at 165° C., and held in a gas stream heated at 400° C. A glow shows the presence of platinum group metals. In the absence of osmium and ruthenium the catalyst should be heated at 400° C. and the glow test tried, both previous to and after washing.

The above procedures were devised to make the glow test reliable as a test for platinum group metals and can, of course, be changed if any of the interfering substances are known to be absent.

Although other methods may be used to remove interfering elements (in which case the regular Curtman and Rothberg

method may be used, except for osmium and ruthenium) they all are rather involved and require the greatest care to insure the complete removal of copper, nickel and cobalt.

SUMMARY.

(1) The theory of contact catalysis and the factors which influence the glow reaction are discussed.

(2) Experiments are described which investigate the factors involving; the nature of the support, heating the catalyst, temperature of gas and catalyst, kind of gas, limit of glow test, and nature of the solutions. Curtman and Rothberg's method may be applied safely, only in the absence of copper, cobalt, nickel or silver.

(3) A modified procedure is given which makes the glow reaction a more reliable test for the platinum group metals.

A Comparison of the Minimum Temperatures as Recorded by Grass Minimum Thermometers Set over Shingle and Grass at Felixstowe. C. W. LAMB. (*Quarterly J. Roy. Meteorological Soc.*, Oct., 1926.)—The two thermometers were 25 yards apart, one placed over glass with shingle for subsoil, the other over bare shingle. The mean daily differences for the months of the year 1926 are as follows, where – means that the grass was warmer and + that the shingle was warmer:

Jan.	Feb.	March	April
−.7°	−.4°	+.1°	+.7°
May	June	July	Aug.
+.3°	+.4°	−.1°	+.2°
Sept.	Oct.	Nov.	Dec.
−.2°	−.2°	−.4°	−.8°

The degrees are Fahrenheit. "There is a higher mean minimum temperature over the shingle than over the grass during the period March–August and *vice versa* during the period September–February." July is an exception to this rule. For the year as a whole the temperature over the glass was .1° warmer than over the shingle. "During the period of long days and short nights (*viz.*, March–August) the time of taking up heat is longer than the time of giving it up, and the actual balance of heat at night is with the shingle. During the period of short days and long nights (*viz.*, September–February) the balance is with the grass," since shingle is a better absorber and a better radiator than grass. G. F. S.

An Absolute Method for Measuring the Velocity of Fluids. H. E. HARTIG and H. B. WILCOX. (*Phys. Rev.*, March, 1927.)—In a tube of infinite length filled with air let two sources of sound emit waves of equal amplitude. In the region between the sources the two sets of waves will interfere and standing waves will be established. At regular intervals there will be planes of zero pressure variation or anti-nodes. If now the air be set in motion the anti-nodes will be shifted in the direction of its flow. From their change in location the velocity of the air can be calculated.

When this method was put into concrete form and tried it gave satisfactory results. The pipe containing the air was 42 feet long and 4 inches in diameter. Air currents of two different velocities gave shifts of the anti-nodes amounting to .904 and 1.859 cm., respectively. From these data the velocities were computed to be 94.2 and 193.5 cm./sec. For the same velocities the smoke drift method gave 95.4 and 195.0 cm./sec. Work is under way to extend the method to the measurement of the velocity of water. In the experiments with air no difficulty occurred that was attributable to turbulence of flow. G. F. S.

THE INDEX OF REFRACTION AND DIELECTRIC CONSTANT OF WATER VAPOR.

BY

ARTHUR BRAMLEY, Ph.D.

Bartol Research Fellow.

BARTOL RESEARCH FOUNDATION
Communication No. 13.

THE recent work of the writer [1] and Wolf [2] on the anomalous behavior of the dielectric constant of bromine and water vapor, respectively, shows that the dielectric constant of these two vapors depends on the temperature and electric field in a manner that indicates that these two phenomena arise through the dependence of the probability of transition and life of the excited molecule on the temperature and electric field, the dielectric constant K being given according to Kramer's formula by the expression,

$$\frac{K-1}{K+2} = \alpha N \sum_{s=1}^{\infty} \sum_{p=1}^{\infty} A_{sp}\, \tau_{sp}\, \lambda^2_{sp},$$

where A_{sp} and A_{ps} represent the probability of transition from the state s to a lower or higher energy state p with emission or absorption of energy, τ_{sp} the life of the excited state s for the frequency ν_{sp}, λ_{sp} the wave-length of the light emitted in the transition from the state s to the lower state p, N the total number of molecules per c.c. and α a constant.

Since the index of refraction n for the wave-length λ is given by the analogous formula

$$\frac{n^2-1}{n^2+2} = \alpha N \sum_{s} \sum_{p} A_{sp}\, \tau_{sp}\, \frac{\lambda^2_{sp}\lambda^2}{\lambda^2 - \lambda^2_{sp}},$$

the index of refraction ought to depend on the temperature and field strength in an analogous manner to that of the dielectric constant.

Using an interferometer method, a study was made of the variation of the index of water vapor with the voltage applied to a cylindrical condenser. The effect observed, which was proportional to the square of the electric intensity, agreed well with the predicted effect but could not be accounted for by the change in density due to the electrostriction effect.

[1] JOUR. FRANK. INST., Feb., 1927.

[2] *Phy. Zeit.*, 27, 1926.

The same method was used to measure the change in the refractive index of air at atmospheric pressure and mercury vapor at a pressure corresponding to room temperature, but no effect was observed with fields up to 50,000 volts per cm.

DESCRIPTION OF APPARATUS.

For the measurement of the variation of the index of refraction of water vapor with electric field, an interferometer method was employed.

The apparatus (Fig. 1) consists of a Michelson interferometer—two full-silvered mirrors M and M^1 and one half-silvered mirror B—in one arm of which was placed the cell C. This cell consists of a cylindrical condenser—diameter of outer cylinder three cm. and of inner .02 cm.—contained in a glass tube with two optical glass end-plates cemented on the ground ends of the tube, the light beam passing through the cell parallel to the axis

FIG. 1.

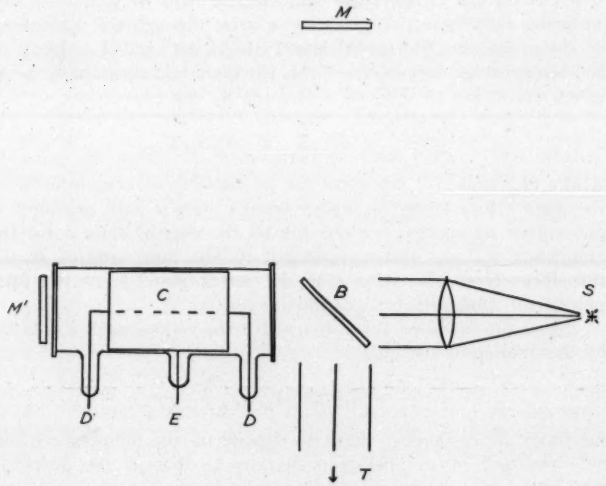


Diagram of apparatus where D and D are the connections to wire used as inner cylinder and E the connection to outer cylinder.

so that the effect could be observed at various positions relative to the inner wire (cylinder). The fringe system was observed through the telescope T; by setting the cross-hair of the instrument on one of the fringes of the system an accuracy of less than one-twentieth fringe shift could be obtained. As a source of light for the interferometer, a quartz-mercury arc was used, from whose spectrum the green line 5461 A was selected by means of Wratten ray filters as a convenient source of monochromatic illumination.

As this method consists of measuring the change in the index of refraction of the vapor with regard to a certain line when the electric field is applied, the relation between the relative fringe shift and the change in the refractive index must be known. If n is the refractive index, λ the wave-length of the light, l the length of the condenser and f the fractional fringe shift, then

$$\delta n = \frac{\lambda f}{2l}. \qquad (1)$$

THEORETICAL DISCUSSION.

On account of the high electric field near the inner cylinder, in this case over 75,000 volts per cm. for vacuum conditions, the conduction current between the two condenser plates, which is considerable, will have to be taken into account in the calculation of the distribution of the electric intensities and voltage between the two electrodes.

Taking Poisson's space charge equation for cylindrical coördinates which is of the form

$$\frac{d}{dr}\left(r\frac{dV}{dr}\right) = -4\pi\rho r = -\frac{2i}{u} \qquad (2)$$

where V is the potential, ρ the space charge per unit volume, i the current flowing between the two cylinders and u the velocity of advance of the ions in the direction of the electric intensity $\frac{dV}{dr}$, and substituting into equation (2) the expression for u in terms of the electric field

$$u = \bar{u}\sqrt{\frac{dV}{dr}}$$

we obtain finally the expression

$$\frac{d}{dr}\left(r\frac{dV}{dr}\right) = -\frac{2i}{u}\frac{1}{\sqrt{\frac{dV}{dr}}} = \frac{A}{\sqrt{\frac{dV}{dr}}}$$

where [3]

$$A = -\frac{2i}{u}.$$

By integrating this equation, we get a relation between $\frac{dV}{dr}$ and r of the form

$$A - \left(\frac{dV}{dr}\right)^{\frac{1}{2}} = \left(\frac{r}{c}\right)^{-\frac{3}{2}}$$

where c is an integration constant, or

$$\frac{dV}{dr} = A^{\frac{1}{2}}\left[1 - \left(\frac{a}{r}\right)^{\frac{3}{2}}\right]^{\frac{2}{3}}.$$

If $a \leq r$, then expanding by Taylor's series, we have

$$\frac{dV}{dr} = A^{\frac{1}{2}}\left[1 - \frac{2}{3}\left(\frac{a}{r}\right)^{\frac{3}{2}} - \frac{1}{9}\left(\frac{a}{r}\right)^{3} - \cdots\right] \qquad (3)$$

and integrating in the region of convergence,

$$V = A^{\frac{1}{2}} r\left[1 + \frac{4}{3}\left(\frac{a}{r}\right)^{\frac{3}{2}} + \cdots\right] \qquad (4)$$

$$+ \text{constant}.$$

For values of $r \gtrless a$ the expansion in the form (3) is no longer valid. In this case, however, the expansion in series of the form

$$\frac{dV}{dr} = A^{\frac{1}{2}}\frac{a}{r}\left[1 - \frac{2}{3}\left(\frac{r}{a}\right)^{\frac{3}{2}} \cdots\cdots\right] \qquad (5)$$

gives by integration,

$$V = A^{\frac{1}{2}} a\left[\log r - \frac{4}{3}\left(\frac{r}{a}\right)^{\frac{3}{2}} \cdots\cdots\right]$$

$$+ \text{constant},$$

and allows the electric intensity and the potential to be evaluated.[4]

[3] Loeb, "Kinetic Theory of Gases," pp. 448 and 503, for values of mobility in terms of the electric field.

[4] W. H. McCurdy, *Phys. Rev.*, Feb., 1926.

From the boundary conditions, (1) that the difference of potential between the two concentric cylinders is V_o and (2) that the capacity of the condenser containing water vapor is 2.3 times the value when the cell is evacuated, we can determine the constants of integration uniquely, provided we can solve the resulting algebraic equations, the constant A being determined from the value of the conductivity of the cell.

For large values of r, we have, making the substitution $r = \frac{3}{2} - \Delta$ where Δ represents the distance from the outer cylinder,

$$E = \frac{dV}{dr} = A^{\frac{1}{3}}\left[1 - \frac{2}{3}\left(\frac{2a}{3 - 2\Delta}\right)^{\frac{1}{3}} \cdots\right]$$

$$= A^{\frac{1}{3}}\left[1 - \frac{2}{3}\left(\frac{2a}{3}\right)^{\frac{1}{3}}\right] - \frac{2}{3}A^{\frac{1}{3}}\left(\frac{2a}{3}\right)^{\frac{1}{3}}\Delta + \cdots$$

from which we see that the electric intensity varies directly as the distance from the outer cylinder for large values of r.

EXPERIMENTAL RESULTS.

In Table I are given the observed fringe shifts for the mercury line 5461 A, when the tube was filled with water vapor at 26.7 mm. of Hg pressure, against voltage applied between the two concentric cylinders and for various distances from the outer cylinder. For the type of condenser which was used, the diameter of the outer cylinder was 3 cm., while the diameter of the inner was only ¼ mm. The fringe shifts were measured visually in all cases against a cross-hair in the observing telescope.

TABLE I.

Potential Applied.	Fractional Fringe Shift.	Observed at a Distance from Outer Cylinder of
11 e.s.u.	1/7	0
11 e.s.u.	1/14	5 mm.
9.1 e.s.u.	1/10	0

For mercury vapor at the pressure corresponding to room temperature and air at 760 mm. of Hg pressure, no effect was observed for the same applied potentials.

In taking the readings for water vapor, the outer cylinder was always positive, as it was found that the arcing potential was around 3 e.s.u. for the reverse direction of the electric field.

After the light had been passing through the tube for several minutes, the visibility became very poor, due to the formation of tiny water drops which remained suspended in the cell and the electric effect on the index of refraction also vanished, so that the data given above were all taken within five minutes of the starting of the mercury arc, the source of illumination.

DISCUSSION.

The index of refraction, according to Kramer's formula, can be expressed in the following way:

$$\frac{n^2-1}{n^2+2} = \alpha \sum_s \left[\sum_r \frac{N_s A_{r\to s} \lambda^2_{rs} \lambda^2}{\lambda^2 - \lambda^2_{rs}} - \sum_t \frac{N_s A_{s\to t} \lambda^2_{st} \lambda^2}{\lambda^2 - \lambda^2_{st}} \right], \qquad (5)$$

where N_s is the number of molecules in the state S, $A_{r\to s}$ the probability of a transition from the state r of higher energy content than s to s, $A_{s\to t}$ the converse probability and λ_{rs} the wave-length of the light absorbed in this transition while λ_{st} the wave-length emitted during the second type of transfer.[5]

Now the number of molecules in the state S, N_s, at the temperature T and electric intensity E, can be written according to Boltzmann's relation in the form

$$N_s = Ne^{-\frac{\varepsilon_s}{kT} + \frac{\mu_s E}{kT}}$$

where ε_s is the energy of the sth state for vanishing electric field E and μ_s is the average electric moment of the molecule in that state.

The probability of an absorption transition $A_{r\to s}$ can be expressed in the form

$$A_{r\to s} = \alpha_{rs} + a_{rs}$$

where a_{rs} represents the part of the probability function due to the application of the electric field and α_{rs} that due to the spontaneous transition between these states.[6]

Now at low temperatures where the effect of radiant energy on the equilibrium is negligible, we must have a statistical equi-

[5] Kramers, *Nature*, May 10, 1924, and Aug. 30, 1924.

[6] Strictly, allowance should be made also for the change in the energy of the states due to the impressed field, but since the energy change of any one state is negligible in comparison with that of the state itself, we can safely neglect it in the expressions where the energy enters.

librium between the components of the probability due to the applied field, *i.e.*, we may write the a_{rs} in the following form

$$a_{rs} = A^r{}_s(E)\, e^{\frac{\varepsilon_r}{kT} - \frac{\mu_r E}{kT}}$$

where $A^r{}_s$ is a quantity which is independent of the temperature but may be a function of the electric intensity E.[7]

If we substitute the values of N_s and $A_{r \to s}$ into equation (5) for the index of refraction, we obtain the relation existing between n, T, and E:

$$\frac{n^2 - 1}{n^2 + 2} = \beta p \sum_s \left[\Sigma A^r{}_s(E)\, e^{\frac{\varepsilon_r - \varepsilon_s}{kT}} e^{-\frac{(\mu_r - \mu_s)E}{kT}} \frac{\lambda^2{}_{rs}\lambda^2}{\lambda^2 - \lambda^2{}_{rs}} \right]$$

where the remaining terms which increase with increasing temperature do not interest us in this discussion and where

$$\beta p = \alpha N .$$

p = the pressure.
β = a constant.

If we replace $\varepsilon_r - \varepsilon_s$ by its equivalent frequency $\nu(rs)$ which ought to appear in the absorption spectrum

$$\varepsilon_r - \varepsilon_s = h\nu(rs),$$

then we obtain finally the equation

$$\frac{n^2 - 1}{n^2 + 2} = \beta p \sum_s \left[\sum_r A^r{}_s(E)\, e^{\frac{h\nu(rs)}{kT}} e^{-\frac{(\mu_r - \mu_s)E}{kT}} \frac{\lambda^2{}_{rs}\lambda^2}{\lambda^2 - \lambda^2{}_{rs}} \right]. \quad (6)$$

This equation which exists between the index of refraction squared, the temperature and the electric field is of the same form as that between the dielectric constant and the same quantities. In the case of bromine and water, the relation has been verified with regard to the dependence of the dielectric constant on the temperature, and in the case of bromine qualitative data have been found for the variation of the dielectric constant with field intensity.

Before we can apply the theory outlined above to the experimental data, we must find the relation between the relative fringe shift and the quantities appearing in equation (6).

[7] Bramley, JOUR. FRANK. INST., July, 1926.

From equation (1) we have that

$$\delta n = \frac{\lambda f}{2l}.$$

For the case of water vapor, we can write the index of refraction in the form

$$n = 1 + \Delta,$$

where Δ is a small quantity compared with unity, then

$$\delta \log \Delta = \frac{\lambda f}{2l\Delta},$$

or since

$$\frac{n^2 - 1}{n^2 + 2} = \frac{2\Delta}{3} \text{ app.}$$

$$\delta \log \left(\frac{n^2 - 1}{n^2 + 2}\right) = \frac{\lambda f}{3l}\left(\frac{n^2 + 2}{n^2 - 1}\right). \tag{7}$$

From the mode of behavior of the variation of the dielectric constant of HOH with temperature, it was shown that the term with energy corresponding to the absorption band at $\lambda_{rs} = 3.0\,\mu$ predominated over the remainder of the series so that it is legitimate to neglect the other terms in comparison with it.

Comparing equations (6) and (7), we finally arrive at the equation for the variation of the refractive index with electric field:

$$\frac{\lambda f}{3l}\left(\frac{n^2 + 2}{n^2 - 1}\right) = \frac{\delta\left[A'_s(E)\, e^{-\frac{(\mu_r - \mu_s)E}{kT}}\right]}{\left[A'_s(E)\, e^{-\frac{(\mu_r - \mu_s)E}{kT}}\right]}. \tag{8}$$

If we consider first the case that A'_s is independent of the electric field intensity E, we obtain

$$\frac{\lambda f}{3l}\left(\frac{n^2 + 2}{n^2 - 1}\right) = -\frac{(\mu_r - \mu_s)}{kT}, \tag{9}$$

the familiar electrostriction equation for the change in the index of refraction with electric field due to the change in the density of the molecules by the reaction of the electric field on their doublets, with the distinction, however, that whereas in the classical theory we have the value of the average permanent moment of

the molecule, here we have, replacing it, the difference of the average electric moments in the two states r and s for which the line of frequency $\nu(rs)$ is absorbed in the transition between them. The values of μ_r and μ_s appearing in (9) obviously refer to their average moment calculated according to the type of space quantization, or otherwise considered, which does not concern us here. Experiments by W. Kliefoth [8] on the electrostriction effect at high electric fields which show a deviation from the linearity of the effect with E, could be accounted for by the general equation (8) through the effect of the electric field on the distribution of the molecules in the various states s, each with its own distinct electric moment μ_s.

If we substitute into equation (9) the various values given in Table I for the effect of the electric field on water vapor and calculate the moment $(\mu_s - \mu_r)$, we find that the electric moment $\mu_s - \mu_r$ must be of the order of 10^{-16}, approximately, over a hundred times the value for the moment of steam measured by Debye's equation for the dielectric constant. It would seem, therefore, that the effect observed must be due to the dependence of the quantities A^r_s on the electric field E.

Considering then the variation of the A's only and neglecting the variation of the term arising from the effect of the electric moments, we obtain

$$\frac{\lambda f}{3l}\left(\frac{n^2+2}{n^2-1}\right) = \delta \log A^r_s(E).$$

But since f varies as E^2, we obtain through integration

$$A^r_s(E) = \Omega^r_s e^{\omega_{rs} E^2}$$

where Ω^r_s and ω_{rs} are independent of the electric field E and the temperature T but may depend on the energy $\varepsilon_r - \varepsilon_s$ and the moment $\mu_s - \mu_r$. Substituting the above value into equation (6), we arrive at the result that

$$\frac{n^2-1}{n^2+2} = \beta p \sum_s \left[\frac{\sum_r \Omega^r_s e^{\omega_{rs} E^2} e^{h\nu(rs)} e^{-\frac{(\mu_r - \mu_s)E}{kT}} \lambda^2_{rs} \lambda^2}{\lambda^2 - \lambda^2_{rs}} + \cdots \right] \quad (10)$$

Since the quantity $\frac{n^2+1}{n^2+2}$ depends on the number of atoms in the state s, Ns and the probability of transition from the state s

[8] *Zeit. f. Phys.*, **39**, 5–6, 1926.

to the state r, $A_{s\to r}$ we should expect that besides the term $e^{-\frac{(\mu_r-\mu_s)}{kT}E}$ due to the electrostriction phenomenon, there would be terms arising from the dependence of the probability of transition $A_{r\to s}$ on the temperature and electric field.

Substituting the values

$$\lambda = 5461\ A$$

$$f = \frac{1}{7} \text{ for } E = 11 \text{ e.s.u.}$$

$$n = 1.000249 \text{ for atmospheric pressure}$$

and

$$\frac{n^2-1}{n^2+2} = 5.6 \times 10^{-6}$$

into the formula for the relative change in the index of refraction, we obtain

$$\frac{\lambda f}{3l}\left(\frac{n^2+2}{n^2-1}\right) = .2,$$

the sign being indeterminate.

The analogous equation for the dielectric constant corresponding to equation (10) differs from it in that the factor

$$\frac{\lambda^2_{rs}\lambda^2}{\lambda^2-\lambda^2_{rs}}$$

has the value unity.

Since the predominating term is that for which $\lambda_{rs} = 3.0\ \mu$, we obtain for the value of the factor in the present investigation where $\lambda = .546\ \mu$ the value

$$\frac{\lambda^2_{rs}\lambda^2}{\lambda^2-\lambda^2_{rs}} = -.25 \text{ approximately,}$$

so that the relative variation of the dielectric constant with electric intensity for the same field strength as that in the present experiment, namely, $E = 24$ e.s.u., ought to be

$$\frac{\lambda f}{3l}\frac{D+2}{D-1} = .8 \text{ approximately.} \qquad (11)$$

For since the quantities A^1 and a appearing in equation (3) have the values

$$A^1 = 24 \text{ and } a = \frac{1}{4},$$

we find for the electric intensity at the outer cylinder calculated from the equation

$$\frac{\partial V}{\partial r} = A^{\frac{1}{3}}\left(1 - \left(\frac{a}{r}\right)^{\frac{3}{2}}\right)^{\frac{1}{3}},$$

the value of 7200 volts per cm.

Substituting this value into equation (11) we find for the relative change in the dielectric constant per unit e.s.u. field intensity from the equation

$$\frac{\lambda f}{3l}\frac{D+2}{D-1} = \delta \log \frac{D-1}{D+2} = \omega_{rs} E^2$$

the value

$$\omega_{rs} = .0014.$$

As we have no means of comparing this factor with the experimental data, we cannot at present verify the theory in this prediction by the actual observable phenomena. However, the theory presented does enable us to account quantitatively for variation of the index of refraction of water vapor with applied electric field for which the electrostriction effect is unable to account, as it considers only the change in density and not the equally important change in the probability of transition which appears in the Lorentz-Kramer dispersion formula.

The Survey of the Stars. J. H. JEANS. (*Nature*, March 12, 1927.)—When the Gold Medal of the Royal Astronomical Society was awarded to Prof. Frank Schlesinger for his accomplishments in stellar parallax and astronomical photography, it was fitting that a historical survey should be given of the field that the American astronomer has made so peculiarly his own. The first part of the address is of rare literary charm. Then, tribute having been rendered to Urania, the development of the idea of parallax is considered. Ptolemy founded his belief that the earth was the centre about which the celestial spheres turned upon the absence of that parallactic motion which should have manifested itself, if the earth moved. Hooke, Roemer and Bradley all tried in vain to discover displacement of the stars due to the motion of our planet. Suddenly in 1838 the existence of parallax was definitely established and not by a single astronomer but by three working independently, Bessel, Struve and Henderson. These found different parallaxes for 61 Cygni, α Lyræ and α Centauri. Thus these three stars were proved to be at different distances from the earth. Progress in the measurement of additional parallaxes was, however, slow, so slow indeed that in 1901 Simon Newcomb's list of stars with known parallaxes contained only 72, of which 15 were doubtful. Two years after this Schlesinger commenced his publication of parallaxes determined by photographic methods. Seven observatories coöperated in the work with the result that his 1924 "General Catalogue of Parallaxes" lists 1870 stars. Here it is rare that the probable error of a parallax exceeds 1/100 of a second, "the angle subtended by a pin-head at a distance of twenty miles," whereas the average error in Newcomb's time was 1/20 second.

Let a series of spheres be described about the sun as a centre with radii equal to 1, 2, 3, 4, 5, etc., parsecs, the parsec being the distance at which a star has a parallax of one second, viz., 19,100,000,000,000 miles. No star has been found as near to the sun as 1 parsec. Three lie within a radius of 2 parsecs, six within 3 and eighteen within 4 parsecs. If stars are scattered uniformly through space there should be 280 within 10 parsecs of the earth, on the supposition that all have been found that exist within a radius of 4 parsecs of the sun, but of these 280 Schlesinger's catalog contains only 86. Likewise within a radius of 100 parsecs 281,250 stars should be situated. "At the present rate of progress the determination of their parallaxes would occupy astronomy for fully 1000 years to come." G. F. S.

Manganese as a Plant Food.—OSWALD SCHREINER and PAUL R. DAWSON (*Ind. and Eng. Chem.*, 1927, 19, 400–404) find that a manganese salt (*e.g.*, manganous sulphate) must be present in the soil in order to produce normal growth of tomato plants and a crop of their fruit. J. S. H.

NOTES FROM RESEARCH LABORATORY, INCANDESCENT LAMP DEPARTMENT OF THE GENERAL ELECTRIC COMPANY.*

BEHAVIOR OF MOLYBDENUM USED AS RESISTOR IN ELECTRIC FURNACE.

By Henry J. Miller and Marcella Lindeman.

A STUDY was made of the effect upon the behavior and life of molybdenum ribbon used as resistors of different kinds of heat insulation material, heating tubing and gases present in electric vacuum or low-pressure melting furnaces.

The materials used for heating tubing and insulation were magnesite and alumina treated in various ways and mixed with different percentages of kaolin. Small traces of carbon or silicon occurring as contaminations were found to have a very destructive effect upon the resistor ribbons, attacking them chemically, forming carbides or silicon compounds. These compounds were found as inclusions at the grain boundaries and caused the ribbons to become hard, brittle and subject to buckling and cracking when heated. Ribbons having long life were always found to be ductile, and to possess large grain-size, showing freedom from impurities, the surface grains being exaggerated in size, perhaps due to their formation from the final reduction of easily fusible molybdenum oxides formed upon first heating the furnace.

Red phosphorus, carbon monoxide, all hydrocarbons and nitrogen from commercial tanks containing oxygen as an impurity were found to harden the molybdenum. Water gas and nitrogen freed from oxygen made the ribbon ductile. Water vapor, sulphur dioxide and sulphur produced no change. Molybdic acid vapor made previously hardened ribbon ductile.

It was found that best results were obtained with molybdenum wound furnaces:

(1) If the first heating of the furnace was carried out under high hydrogen pressure.

* Communicated by the Director.

(2) If the heating tubing and insulation were of calcined pure alumina mixed with aluminum hydroxide as binder and fired at 1500° C.

(3) When the material contained carbon, if oxides of high degree of oxidation were added to react with the carbon, the products of reaction being removed by evacuation, or the molybdenum ribbon was coated with low oxides to prevent oxidation or carbonization.

NOTES FROM LIGHTING RESEARCH LABORATORY, NATIONAL LAMP WORKS OF THE GENERAL ELECTRIC COMPANY.*

DEFINING GLARE AND VISIBILITY.

By M. Luckiesh.

Director, Lighting Research Laboratory.

THE inadequacy of our knowledge pertaining to glare and visibility has naturally been accompanied by a lack of standardization of terms and a general looseness of expression. In differentiating and defining these terms we might begin by distinguishing between cause and effect. When we think of glare are we not immediately and primarily conscious of *ourselves* and of *our bodily comfort?* If so we may speak of the glare *from* a lighting condition. On the other hand, when we think of visibility are we not immediately and primarily conscious of the object? If so, we may speak of the visibility *of* the object.

With the aid of Dr. P. W. Cobb the writer has proposed certain definitions [1] based upon the following brief though less concise statements:

Glare is a name preferably confined to a certain factor in lighting situations which gives rise to expressions of discomfort, distraction, irritation or pain from the person exposed, referable to brightness in the visual field which is absolutely or relatively high. Lowered visibility is not characteristic of glare, although it may be present in some cases; and glare is sometimes more in evidence when close visual work is under way. In general, glare may be held to consist of responses to undetermined physiological disturbances within the organism, rather than to be referable to its orderly adjustment to external objects, as is the case of "seeing" or visibility.

Visibility in current dictionaries is defined as the state, quality, capability of being seen; and "seeing" can be appraised in no other way than by the behavior of the subject who is supposed to

* Communicated by the Director.

[1] To appear in *Trans. Illuminating Eng. Soc.*

see, whether his response is appropriate or not. In a single trial, his response is either *all* appropriate; or it is not; or he refuses to respond. In a number of trials under like conditions we may get all three responses. There would seem no escape then from the definition of visibility in any particular situation as the statistical ratio of the number of times "seen" (*not guessed right*) to the number of trials.

LUMINOUS EFFICIENCIES OF COMMERCIAL TUNGSTEN LAMPS.

By A. H. Taylor.

IN THE past a number of researches have been carried out to determine the relative visibility of energy of different wave-lengths. These show that for the average observer monochromatic radiation of wave-length approximately 555 mμ has the highest luminous efficiency. Ives,[2] reviewing the results of various researches, finds the least mechanical equivalent of light to be 0.00161 watt per lumen, or an efficiency of 621 lumens per watt.

No light-source has been found which will emit all its energy in the visible spectrum, hence none of them approaches the luminous efficiency of monochromatic radiation of maximum luminosity. Indeed, such a light-source would be very unsatisfactory, for it would not reveal colors in objects illuminated. In order to bring out the true colors of objects, the light should contain all wave-lengths of the visible spectrum. The ideal light-source would give white light, of the same spectral distribution as the radiation from a theoretical "black-body" at temperature 5250° K. This is approximately the color of noon sunlight in June. All incandescent lamps operate at temperatures much below this, hence their light has a deficiency of blue and excess of red when compared with white light. A "black-body" at temperature 5250° K. would have a luminous efficiency only 12.5 per cent. of that of a monochromatic light of wave-length 555 mμ. The following table compares the efficiencies of several sizes of the present commercial tungsten lamps with a "black-body" at 5250° K.

[2] Ives, *Jour. Opt. Soc. Am.* and *Rev. Sci. Inst.*, Feb., 1926, p. 75.

Relative Luminous Efficiencies of White Light and Commercial Tungsten Lamps.

Light-source.	Lumens per Watt.	Relative Efficiencies. Per cent.
Black-body * at 5250° K. (white light)	77.6	100
1000-watt projection tungsten lamp	26.8	34.5
500-watt gas-filled tungsten lamp	19	24.5
100-watt gas-filled tungsten lamp	13.2	17.0
50-watt gas-filled tungsten lamp	10.3	13.3
25-watt vacuum tungsten lamp	9.4	12.1

* Approximately same color as noon sunlight in June.

Volumetric Determination of Zinc.—W. H. CONE and L. C. CADY, of the University of Idaho (*Jour. Am. Chem. Soc.*, 1927, **49**, 356–360), recommend diphenylbenzidine as an internal indicator in the volumetric determination of zinc by titration with potassium ferrocyanide. The indicator is prepared by solution of one grain of diphenylbenzidine in 100 c.c. of concentrated sulphuric acid; several drops of this indicator are used in each titration. The standard ferrocyanide solution contains 22 grams of potassium ferrocyanide and 0.3 gram of potassium ferricyanide in each litre. During the titration, a blue color develops, and changes to a purple, and becomes a pale green at the end point. In the presence of zinc salts, the ferricyanide oxidizes the diphenylbenzidine to a blue quinone salt, and this salt is reduced as soon as an excess of ferrocyanide is present. The titration is made in the presence of sulphuric acid. Diphenylamine may be used instead of diphenylbenzidine.

J. S. H.

A Method for Measuring Thermal Expansion Coefficients by the Use of Photographic Registration with X-rays. KARL BECKER. (*Zeit. f. Physik.*, **40**, Nos. 1 and 2.)—In the Debye-Scherrer method here employed two X-ray impressions are taken simultaneously on the same film, one with the substance at room temperature, the second with it at some higher temperature. From a study of the two figures thus produced the linear expansion coefficient can be calculated. The following results were obtained:

Substance.	Temperature Range.	Linear Expansion Coefficient.
Tungsten	18° to 2200° C.	7.5×10^{-6}
Tungsten	18° to 1750° C.	6.6×10^{-6}
Tungsten	18° to 1380° C.	5.8×10^{-6}
ZrO_2	18° to 1300° C.	4.5×10^{-6}
Silicon	18° to 950° C.	3.55×10^{-6}
Carborundum	18° to 1200° C.	6.25×10^{-6}

The increase in the coefficient of tungsten with elevation of temperature is noteworthy. G. F. S.

Second Coal Conference.—A second international Conference on Bituminous Coal will be held at the Carnegie Institute of Technology in November of 1928. The first conference was called by President Baker of the Institute for the purpose of finding new uses for bituminous coal and especially to discuss the problem of liquefying coal to supplement the petroleum oil supply of the world. More than 1700 delegates, including representatives of thirteen different countries, attended. The speakers included Dr. Friedrich Bergius and Prof. Franz Fischer, who have successfully liquefied coal; General George Patart and Jean Bing, of France; Dr. C. H. Lander, Geoffrey M. Gill, Harald Nielsen, and Dr. R. Lessing, of England; and several other well-known foreign scientists in addition to a long list of prominent American engineers and men of affairs and science.

NOTES FROM THE RESEARCH LABORATORY, EASTMAN KODAK COMPANY.*

REFLECTION CHARACTERISTICS OF PROJECTION SCREENS.[1]

By L. A. Jones and C. Tuttle.

THE reflection characteristics which are desirable in order that the projection screen shall be adapted to an auditorium of given dimensions are pointed out. The distribution of reflected light should be such that for no angle of observation is the brightness greater than four times that at any other angle of observation in the theatre. Non-uniformity of screen brightness for an observer from a single point is due to difference in angle of observation of the right and left-hand edges of the screen. Since this angular difference is a maximum for observers on a line perpendicular to one side of the screen, the effect is just as serious for a narrow house as for a wide one. A criterion for this non-uniformity tolerance is the brightness ratio of 0° to 40° observation. It is suggested that this ratio ought not exceed ten. Data showing the distribution of reflected light for normal incidence and 0° to 50° observation are presented. Most of the projection screens manufactured at present are included in the forty surfaces that were measured.

* Communicated by the Director.

[1] Communication No. 295 from the Research Laboratories of the Eastman Kodak Company and published in *Trans. Soc. Mot. Pict. Eng.*, 10, No. 28, 1926, pp. 186–194.

Inversion of Magnetic Inclination. P. M. MERCANTON. (*Terrestrial Mag. and Atmospheric Elec.*, Dec., 1926.)—Volcanic lavas upon cooling in the magnetic field of the earth assume a magnetic condition that is very permanent though weak. An examination of lavas at the present time consequently furnishes information regarding the direction of the earth's field at the time and place where solidification occurred. Chevallier has shown that such a study provides very definite knowledge of the declination prevalent when the various lavas of Mount Etna became solid. The data relating to inclination are less clear, but they can be depended upon if they indicate as great a change as an actual reversal of the terrestrial field.

The author examined the permanent magnetism of specimens of tertiary igneous rock from Spitzenbergen and Greenland and found that the lower parts were of south polarity. On the other hand, lava two centuries old from Jan Mayen Land had the opposite polarity. A similar study of rocks from the southern hemisphere of the earth failed to reveal an inversion of inclination. If this great difference in the history of the two hemispheres should be confirmed by subsequent investigations, it will mean that the magnet-poles have shifted their position greatly. This may be connected with the change in the axis of rotation claimed by Wegener. G. F. S.

Experiments to Test the Possibilities of Transmutation by Electronic Bombardment. M. W. GARRETT. (*Proc. Roy. Soc.*, A 767.)—The author has already repeated with negative results the procedures by which Miethe and Stammreich, as well as Nagaoka, claimed to have produced gold from mercury. He reports in this paper his endeavor to transmute tin into indium. The latter as a product of transmutation would have at least two advantages. Even a minute trace can be detected spectroscopically and, in addition, it is of such rare occurrence that there is little chance of its getting into the experiment by contamination from surrounding materials.

It was found that pure tin freed completely from its oxide could not be used because it adhered so tightly to the walls of the quartz tube as to crack it upon cooling. Furthermore, it was hard to get a sample of tin that showed no trace of the blue indium line. However, after passing 18 amperes for fifty hours through the tube, no spectroscopic evidence of the formation of indium could be detected. In another experiment titanium was bombarded by electrons *in vacuo* but no trace of scandium was obtained. G. F. S.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

SUGAR TOLERANT YEASTS IN CHOCOLATE-COATED CREAMS.[1]

By M. B. Church, H. S. Paine, and J. Hamilton.

[ABSTRACT.]

THOUSANDS of dollars are lost to candy manufacturers yearly through the bursting of chocolate-coated cream-centre candies. The Bureau of Chemistry has found that yeasts of high sugar tolerance are capable of active growth in the cream centres and cause bursting through the formation of gas. Proper sanitary conditions at the factory, the use of sound ingredients, and the use of a cream of high syrup density, when permitted by the character of the cream, will reduce this trouble.

NAPHTHALENE SULPHONIC ACIDS VII—HYDROLYSIS OF NAPHTHALENE-1, 6-DISULPHONIC ACID.[2]

By J. A. Ambler and J. T. Scanlan.

[ABSTRACT.]

NAPHTHALENE-1, 6-disulphonic acid was prepared, isolated from its isomers, and crystallized as the free acid. This acid was heated in sealed Pyrex tubes with concentrations of sulphuric acid ranging from 1 to 85 per cent. and at temperatures ranging from 100° C. Quantitative determinations were made of the degree of hydrolysis over the entire range within which any change without charring was observed and the results were tabulated. The reaction products were determined qualitatively wherever any change occurred. The temperature at which hydrolysis begins in each concentration of sulphuric acid used was recorded.

From the results obtained the following general rule may be deduced: Naphthalene-1, 6-disulphonic acid, when heated until equilibrium is reached with a concentration of sulphuric acid not sufficiently high to sulphonate naphthalene at the temperature employed and at a temperature sufficiently high to hydrolyze the 1,6 acid, is converted directly into naphthalene. If, however, the temperature is high enough to hydrolyze the 1,6 acid and the

* Communicated by the Chief of the Bureau.

[1] Published in *Ind. and Eng. Chem.*, **19**, No. 3, pp. 353–358.

[2] Published in *Ind. and Eng. Chem.*, **19**, No. 3, pp. 417–421.

sulphuric acid concentration is sufficient to sulphonate naphthalene at the temperature used, isomeric disulphonic acids are produced. Their nature and relative proportions are determined by the ratio of sulphuric acid to sulphonic acid, the strength of the sulphuric acid, and the temperature. The resulting acids are the same as would be obtained by the direct sulphonation of naphthalene under identical conditions.

The naphthalene-1, 6-disulphonic acid cannot exist under the conditions of vapor phase sulphonation of naphthalene, as this reaction is carried out in an open system at 220–245° C. and with sulphuric acid having a concentration of 80 to 95 per cent.

In the steam treatment for the elimination of tar, which is carried out at a temperature slightly above 100° C. in 10 per cent. sulphuric acid, the 1,6 acid is not affected.

MEANS FOR PREVENTING "EXPLOSIVE" OR BURSTING FERMENTATION OF CHOCOLATE-COATED FONDANT CANDY.[1]

By H. S. Paine, V. Birckner and J. Hamilton.

[ABSTRACT.]

BURSTING fermentation of chocolate-coated fondant confectionery, which causes a large financial loss each year and which is due to the action of highly sugar-tolerant yeasts, may be prevented by adding a suitable proportion of the enzyme invertase to the fondant before the fondant centres are molded. The invertase, by inverting a portion of the sucrose present and thereby increasing total sugar solubility, causes such an increase in the density and osmotic pressure of the syrup phase of the fondant as to render it resistant to fermentation. The critical solid content is about 79 per cent. Fondants containing a syrup phase with a higher solid content were practically free from fermentation.

Fondants containing imbedded fruit present a special case, owing to decrease in density of syrup of the fondant as a result of diffusion of fruit juice. Preliminary heating of the fruit at boiling temperature for periods which did not cause injury to flavor and texture retarded, but did not prevent, fermentation. A combination of preliminary heating and the use of a liberal proportion of invertase satisfactorily prevents fermentation in confectionery of this type.

[1] Published in *Ind. and Eng. Chem.*, 19, No. 3, pp. 358–363.

NOTES FROM THE U. S. BUREAU OF MINES.*

RECOVERY OF FINE MICA.

By W. M. Meyers.

In a recent study of the ground mica industry, I was impressed with the waste of mica incurred through incomplete settling of fine material, and its irrecoverable loss when carried away in the waste water. As finely ground mica is worth over $100 a ton, the bureau has conducted a study to decrease the loss of fine mica. Laboratory tests were conducted which indicate that the use of flocculating reagents may solve the problem. The properties of electrolytes and their application in flocculating fine materials in clays is well known, and the method has also been used with some success on ore slimes. The experiments show that a number of reagents are suitable in settling fine mica, but sulphuric acid, aluminum sulphate, and potash alum appear to be the most suitable. Further information will be found in Serial 2798, recently published by the Bureau of Mines.

METHOD FOR SEPARATING HYDROCARBONS IN COAL GAS.

By F. E. Frey and W. P. Yant.

Practical distillation is an essential process in the analysis of gaseous hydrocarbons in coal gas, vapors of gasoline, and various other commercial gases and vapors, because the close similarity of the commercial composition of the hydrocarbons makes chemical analyses unsatisfactory. Fractional distillation has been found especially useful in determining the composition of coal gas in analytical work of the Bureau of Mines. A method has been developed in the bureau's laboratories whereby the individual saturated and unsaturated hydrocarbons in coal gas can be accurately determined. It was found that the boiling-point of the different hydrocarbons—methane, ethylene, ethane, propylene, propane, butylene and butane—mostly depends upon the number of carbon atoms contained in a molecule of the substance, and is affected very little by differences in structure and unsatur-

* Communicated by the Director.

ation. The method involves supplementing the usual Orsat analysis by fractional distillation, and can be applied to very small samples, only 50 to 2000 cubic centimetres of the gas being required. A more complete description will appear in *Industrial and Engineering Chemistry*.

FLOTATION OF OXIDIZED ORES.

By Thomas Varley.

THE Bureau of Mines, in 1916, made public the results of experimental work it had conducted on the flotation of oxidized ores. At that time, treatment of sulphide ores by flotation was established in metallurgical practice, but the treatment of oxides by flotation was still in its infancy. Since that time, some of the most important mining companies of the western United States and Mexico have put into practical operation plants for the flotation of oxidized ores. Much oxidized ore is being smelted directly, but it is expected that flotation will continue to make gains as improvements on the method are developed. Detailed information on practice in most plants employing the process was obtained. It was found that flotation plants treating oxidized ores have adopted largely the reagents used in floating sulphides, and that in general, special reagents developed for oxidized ores by commercial laboratories are not as yet being extensively used in plant practice. The percentage of metal content recovered in oxidized ores has not greatly increased since 1916, but the growth is rather in the increase of tonnage treated. In view of the fact that developments in sulphide practice have been followed, rather than developments from research on oxidized ores, there is a promising field for further research on the oxidized ores. A more detailed report is being published as a serial by the Bureau of Mines.

RAILROAD FUEL OIL CONSUMPTION.

By E. B. Swanson.

A SERIES of studies, relating to the consumption of fuel oil in the United States, has been conducted by the Bureau of Mines in coöperation with the American Petroleum Institute. In the course of the work, a study was made of use of fuel oil by railroads. Railroad fuel oil purchases account for approximately

one-fifth of the total fuel oil marketed annually in the United States. During 1925, purchases totalling 70,636,559 barrels were made by 147 railroads. Of the total purchased, 69,461,119 barrels were consumed and 1,175,440 added to the quantity in storage. Railroad stocks of fuel oil at the end of the year amounted to 15,001,647 barrels, as compared with 11,826,207 barrels at the beginning of the year. Of the total consumed, 59,627,639 barrels were burned as locomotive fuel and 9,835,480 barrels were consumed in shops, power plants, ferry boats and other non-locomotive uses. A more complete statement will be found in Information Circular 6017.

The Transverse Thermo-electric Effect in Metal Crystals. P. W. BRIDGMAN. (*Proc. Nat. Acad. Sciences,* Feb., 1927.)—In 1851 Lord Kelvin made this prediction: "If a bar of crystalline substance possessing an axis of thermo-electric symmetry has its length oblique to this axis, a current of electricity sustained in it longitudinally will cause evolution of heat at one side and absorption of heat at the opposite side, all along the bar, when the whole substance is kept at one temperature." Voigt in 1910, basing his opinion upon his equations, gave his adhesion to the existence of such an effect. Until Bridgman took up the matter it seems that no one had investigated it. He has discovered the effect in bismuth, zinc, tin and cadmium, using in all cases bars consisting of single crystals and measuring 10 cm. in length and 6 mm. in diameter.

He used three bismuth bars. In two the basal planes were inclined 20° to the length and in the third it was parallel to the length. The current entered and left by clamps fixed to the two ends of the bar. The temperature difference between the two sides was measured by thermo-elements. When a current of the order of 1 ampere flowed through the bar the difference of temperature between the two sides was about .4° C. When the direction of the current was reversed, the side of the bar that had been the hotter became the cooler and *vice versa*. The temperature difference seemed proportional to the current strength. It changes in sign if the bar be rotated through 180° without any change in the location of the thermocouples. It does not vary with the position of these along the bar. Thus the whole of one side is cooled while the whole of the other side is warmed. In zinc, calcium and tin the effect was much less.

The author maintains that both Voigt and Lord Kelvin made mistakes in the arguments that led them to expect the effect that he has discovered experimentally. G. F. S.

Yearly Variation of the Quantity of Ozone in the Upper Atmosphere. F. W. P. GOETZ. (*Beitr. z. Physik. d. f. Atmosphære,* 13, No. 1.)—"Wave-length 320 $\mu\mu$ is the farthest outpost of the solar spectrum, thrust forward like an island into the region where ozone absorbs the radiation." The author makes a study of the intensity of the radiation of this wave-length received from the sun by means of what he designates Filter Cd 320 $\mu\mu$, which seems to be a combination of a cadmium photo-electric cell with a filter permitting only a narrow portion of the spectrum in the designated region to pass, and deduces the quantity of ozone present in the upper air. The relative amounts of this substance in the four seasons are, in arbitrary units, 1922, winter, 97; spring, 112; summer, 95.5; autumn, 92; and 1923, winter, 103.5; spring, 115. He finds that Suering's observations indicate a similar annual change.

At Arosa, where his laboratory is situated, changes in atmospheric pressure and in ozone content take place in opposite directions.

G. F. S.

THE FRANKLIN INSTITUTE.

(Proceedings of the Stated Meeting Held Wednesday, April 20, 1927.)

THE regular monthly meeting of the Institute was held Wednesday, April twentieth, at eight-sixteen P.M., with the President, Dr. Wm. C. L. Eglin, presiding.

The Secretary reported that the minutes of the preceding meeting had been published in full in the April JOURNAL, and moved that they be approved as printed. No objection being offered, the President declared that the minutes were thus approved.

The Secretary announced that since the last meeting of the Institute there had been ten additions to the membership of the Institute—six Resident members and four Non-resident members; and one substitution in one of the Contributing memberships.

He announced, also, with regret, the death of two members.

There being no further business, the President presented as the lecturer of the evening Mr. A. H. Markwart, Vice-president, Pacific Gas and Electric Company, who read an important paper upon the subject of "Power in California." The paper was followed by an animated and interested discussion.

The meeting adjourned at nine-forty P.M., with a hearty vote of thanks to Mr. Markwart.

HOWARD MCCLENAHAN,
Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting Held Wednesday, April 6, 1927.)

HALL OF THE COMMITTEE,
PHILADELPHIA, April 6, 1927.

MR. M. M. PRICE, *in the Chair.*

The following reports were presented for first reading:

No. 2858: Thurlow Backwater Suppressor.
No. 2869: Eppley Standard Cell.
No. 2870: Work of Dr. Edward Leamington Nichols.

GEORGE A. HOADLEY,
Secretary to Committee.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, April 13, 1927.)

RESIDENT.

MR. JOHN K. FRANCIS, Draftsman, Baldwin Locomotive Works. For mailing: 536 North Nineteenth Street, Philadelphia, Penna.

MR. LESLIE GRISCOM, Mechanical and Electrical Engineer, John Lang Paper

Company, 24th and Wood Streets. For mailing: 5332 North Camac Street, Philadelphia, Penna.

MR. WILLIAM A. HEILPRIN, Machinery Merchant and Engineer, 124 North Third Street, Philadelphia, Penna.

MR. JOSEPH S. PECKER, Mechanical Engineer, 706 Chestnut Street, Philadelphia, Penna.

MR. WILLIAM E. RICHARDSON, Radio Mechanic, 611 Market Street. For mailing: 5449 Locust Street, Philadelphia, Penna.

MR. CHARLES A. STANWICK, Engineer, 1600 Walnut Street, in care of Day and Zimmermann, Philadelphia, Penna.

NON-RESIDENT.

MR. LUCIUS B. ANDRUS, Guaranty Building, Indianapolis, Ind.

DR. HERBERT A. CLARK, Physicist, in care of Taylor Instrument Companies, 93 Ames Street, Rochester, N. Y.

MR. ANDREW FLEMING, Merchant, 81/8 Bentinck Street, Calcutta, India.

MR. ARTHUR F. POOLE, Engineer, in care of Morse Chain Company, Ithaca, N. Y.

CONTRIBUTING.

MR. WILLIAM ADAMS, The Ajax Metal Company, Frankford Avenue and Richmond Streets, Philadelphia, Penna.

CHANGES OF ADDRESS.

MR. MAURICE C. BURTON, The Wood-Norton Apartments, C-1, Germantown, Philadelphia, Penna.

MR. CLARK DILLENBECK, 518 East Mermaid Lane, Chestnut Hill, Philadelphia, Penna.

MR. JOHN M. HAMMOND, The Phototechnical Laboratory, 703 14th Street, N. E., Washington, D. C.

MR. RICHARD P. HARVEY, Hotel Medford, Milwaukee, Wis.

MR. J. HALMER HAYNER, 7000 Lincoln Drive, Lincoln Terrace Apartments, Philadelphia, Penna.

MR. JOHN C. KUBALE, 141 Trafalgar Street, Rochester, N. Y.

MR. NOEL T. WELLMAN, 21–23 Prospect Street, East Orange, N. J.

NECROLOGY.

Edwin Swift Balch, a benefactor of the Institute, for ten years a member of its Board of Managers and for fourteen years active on the Committee on Library, died on March 15th. Mr. Balch graduated from Harvard University in 1878, later studied law and was admitted to the bar in 1882. He was greatly interested in geographical and geological subjects and is the author of about a dozen volumes on mountain exploration, ice caves and the North and South Poles, as well as of numerous communications on the subjects to learned societies. Mr. Balch was a member of the leading geographical and geological societies of the world. His membership in the Institute dates from January, 1897.

Dudley Farrand was born at Bloomfield, N. J., February 21, 1869, and died at Fair Haven, N. J., on March 3, 1927. In 1887, after graduation from the Newark Academy, he became associated with the Newark Electric Light and Power Company and ten years later joined the Peoples Light and Power Company. In 1899 he became General Manager of the United Electric Company of New Jersey. When the Public Service Corporation of New Jersey was formed, Mr. Farrand was made General Manager of the Electric Department, and in 1910 when the Public Service Electric Company was organized, he was made General Manager and five years later was promoted to the position of Vice-president. From 1917 until 1923 he was Assistant to the President of the Public Service Corporation of New Jersey and during the latter year was appointed Vice-president in Charge of Industrial Relations. Mr. Farrand was President of the Newark Safety Council and a member of the Newark Board of Education; he was a member of the National Electric Light Association, the American Institute of Electrical Engineers, the Society of Professional Engineers of New Jersey and several social organizations. He became a member of The Franklin Institute in 1913.

LIBRARY NOTES.

RECENT ADDITIONS.

American Electrochemical Society.—Transactions 1926. Volume 49. 1927.

American Institute of Mining and Metallurgical Engineers.—Transactions. General Alphabetical and Analytical Index. Volumes 56–72, inclusive (1917–1925). 1926.

American Society for Testing Materials.—Proceedings Twenty-ninth Annual Meeting. Volume 26, Parts 1–2. Two volumes. 1926.

Annuaire Sucrier. Volume 53. 1927.

BARRY, T. HEDLEY, DRUMMOND, ALAN A., and MORRELL, R. S.—The Chemistry of the Natural and Synthetic Resins. 1926.

BECQUEREL, JEAN.—Cours de Physique. Two volumes. 1924–1926.

Bulletin Year Book and Almanac. 1927.

Chemical Society.—Annual Reports on the Progress of Chemistry for 1926. Volume 23. 1927.

Chimie et Industrie. Numéros Specials. Congrès de Chimie Industrielle. Four volumes. 1923–1926.

DARROW, KARL K.—Introduction to Contemporary Physics. 1926.

EDER, J. M.—Rezepte, Tabellen und Arbeitsvorschriften für Photographie und Reproductionstechnik. Twelfth and thirteenth edition. One volume. 1927.

ELLIOTT, T. C. J.—The Dial Machine. 1926.

FISCHER, EMIL.—Neuere Erfolge und Probleme der Chemie. 1911.

FISCHER, EMIL.—Organische Synthese und Biologie. Zweite, unveranderte Auflage. 1912.

FISCHER, EMIL.—Untersuchungen aus verschiedenen Gebieten. 1924.

FISCHER, EMIL.—Untersuchungen über Aminosäuren, Polypeptide und Proteine (1899–1919). Two volumes. 1906–1923.

FISCHER, EMIL.—Untersuchungen über Depside und Gerbstoffe (1908–1919). 1919.

FISCHER, EMIL.—Untersuchungen über Triphenylmethanfarbstoffe, Hydrazine und Indole. 1924.

FRIEND, J. NEWTON, Editor.—Text-book of Inorganic Chemistry. Volume 3, Part 2, Beryllium and Its Congeners, by J. C. Gregory and M. S. Burr. 1926.

HAWLEY, L. F., and WISE, LOUIS E.—The Chemistry of Wood. 1926.

Jahrbuch der drahtlosen Telegraphie und Telephonie. Volumes 12–14. 1918–1919.

KUTTNER, JULIUS.—Sketches and Working of Oil Engines. 1926.

LAWALL, CHARLES H.—Four Thousand Years of Pharmacy: An Outline History of Pharmacy and the Allied Sciences. 1927.

MACPHERSON, HECTOR.—Modern Astronomy: Its Rise and Progress. 1926.

NERNST, W.—The New Heat Theorem: Its Foundations in Theory and Experiment. Translated from the second German edition by Guy Barr. No date.

PLANCK, MAX.—Treatise on Thermodynamics. Third edition translated from the seventh German edition by Alexander Ogg. 1927.

POGGENDORFF, J. C.—Biographisch-literarisches Handwörterbuch für Mathematik, Astronomie, Physik, Chemie und verwandte Wissenschaftsgebiete. Band V, 1904–1922. Redigiert von P. Weinmeister. 1926.

POPOFF, STEPHEN.—Quantitative Analysis. Second edition. 1927.

REYMOND, ARNOLD.—History of the Sciences in Greco-Roman Antiquity. Translated by Ruth Gheury de Bray. No date.

SENTER, GEORGE.—Outlines of Physical Chemistry. No date.

Society of Chemical Industry.—Reports of the Progress of Applied Chemistry. Volume 11. 1926.

Society of Dyers and Colorists.—Color Index. Edited by F. M. Rowe. First edition. 1924.

SOUTHALL, JAMES P. C.—Mirrors, Prisms and Lenses. Enlarged and revised edition. 1923.

UNDERHILL, CHARLES R.—Solenoids, Electromagnets and Electromagnetic Windings. Second edition, thoroughly revised. 1921.

BOOK REVIEWS.

HISTORY OF THE SCIENCES IN GRECO-ROMAN ANTIQUITY. By Arnold Reymond. Translated by Ruth Gheury de Bray. x–245 pages, 40 illustrations, small 8vo. New York, E. P. Dutton and Company. Price, $2.50.

Can we moderns estimate correctly the spirit of ancient science? Undoubtedly the scientist who becomes familiar with the records of Greece is struck by the penetration and earnestness with which the "philosophers" pursued their inquiries, but mixed with much that is commendable is a large amount of absurd statements concerning which one wonders how intelligent and observing men could have gone so far wrong. Sydney Smith is credited with an allusion to "those confounded ancients who anticipated everybody," and in many cases such anticipation has really occurred. Probably we may say that the present age exceeds the ancient enormously in knowledge but not in wisdom. Concerning the basic principles of morals and ethics as applied in civilized communities,

ancient statesmen and philosophers knew about as much as we do, but our treasury of facts is many times greater than theirs, and we have been able to apply our knowledge in so many ways that we seem to have a degree of control over nature.

The main difficulty in getting a clear knowledge of the accomplishments and methods of ancient scientists is the small amount of written material that remains. We have a record, for instance, of the service of Sextus Julius Frontinus as water-commissioner of Rome in the reigns of Nerva and Trajan, and we have an account of the water-supply of Rome that is assigned to him. It is very interesting and its Latinity fully corresponds to that of the age in which it purports to have been written, yet the oldest manuscript is of the eleventh century, more than a thousand years after the death of the alleged author. The only manuscript of Tacitus' Annals is also of the same century. Can we trust sources of such late origin, considering the errors that may creep in copying and also the tendency of the ancient and mediæval writers to assign authorship without justification?

Science and art, as we understand the words to-day, find their embryonic forms in Greece. The study of nature for the sake of knowledge and the appeal to the emotions through painting, sculpture, poetry and drama, found their best expressions in that land. Modern civilization in western Europe and America is based for its material nature on Greek thought and for its moral standards on Jewish principles. The two nations differed radically as to their outlook on nature. This is well shown in their respective appreciations of the rainbow. This striking phenomenon excited the investigations of the Greeks, who having no knowledge of the composite nature of white light could not explain the physics of the colors. The Jews did not concern themselves with the nature of the phenomenon. To them the "bow" (the Hebrew word means the weapon) was hung in the sky to proclaim the intention of the Deity, namely, that the war against humanity was over. It was God's weapon hung in the heavens.

Though, as indicated in the title, the book is an exposition of the development of science in Greece and Rome, brief notice is given of the status of mathematical, astronomical, physical and natural sciences in Egypt and Chaldea. Considerable development seems to have occurred in these regions. Among the earliest observations were naturally those relating to the length of the year. The seasonal variations and their fairly regular recurrence must have impressed the earliest human beings. The rising and setting of the stars with the contrast between the fixed arrangement of most of them and the "wandering" of a few are phenomena that must have been very early appreciated.

The bulk of the book is devoted to a detailed presentation of work of the Greek philosophers followed later by the Romans, who derived their science as their other cultures from the Greeks. The period covered is from the earliest records of Greek philosophy (about 650 B.C.) to the sixth century of the present era.

Any one wishing to get a good notion of the ability and services of the ancient philosophers will find this book a most satisfactory aid. It sets forth in clear and attractive form the data at hand and critical judgments thereon. The translation is well done. HENRY LEFFMANN.

OUTLINES OF PHYSICAL CHEMISTRY. By George Senter, D.Sc. (Lond.), Birkbeck College (University of London). Fourteenth edition, xx–421 pages, 13 × 19 cm., 46 illustrations in text. New York, D. Van Nostrand Company, 1926. Price, $3.

As indicated in the title and stated in the preface, this book is an attempt "to provide an elementary introduction to physical chemistry." The purpose of the author has been to present the general principles of the subject in a volume of moderate size. A "five-foot book-shelf" would be necessary to contain all of the recent excellent monographs and manuals describing the various phases of the subject.

Theories of atomic structure, solutions, catalysis, colloids, hydrion concentration and electromotive force were once assigned but few pages of text, but are now highly specialized fields with a voluminous literature. An author or teacher must carefully cull the salient points of the accumulated data to suit the needs of his readers and students. The subject-matter in this text has been arranged in an excellent manner for didactic purposes, which bespeaks the outcome of years of teaching. A commendable feature is the mathematical derivation of the various formulas throughout the text and the selected list of problems and questions in the appendix.

Portions of the text have evidently been written for several years without further revision. Several pages are devoted to a discussion of the periodic table and only two paragraphs are given to the nuclear atom theory and atomic number. Only minor reference is made to Bohr and his theories and to Lewis and his work in this country. The section on colloids should contain more references to recent work, of which there seems to be an unlimited amount available for student use. Hydrion concentration and the use of the hydrogen electrode in electrometric analysis receive scant attention. Ionization constants, solubility products, and the theory of indicators are of sufficient importance to warrant more consideration.

The book is recommended for an introductory course in the subject only, supplemented by reference to books on modern practices and recent scientific journals. GEORGE WESLEY PERKINS.

MESURES ÉLECTRIQUES. Par Jean Granier, Ingenieur, Préparateur à la Faculté des Sciences de Montpellier. 200 pages, 11 × 16 cm., paper. Paris, Librairie Armand Colin, 1927. Price, unbound, 9 francs; bound, 10.25 francs.

An important adjunct in electrical laboratory measurements is a ready means of reference to precise information on methods which may be adopted and apparatus which may be employed for a given purpose. The operator, who is presumably well-informed, may need only a suggestion of what is best adapted to his purpose; or he may desire a brief outline of principle of operation to refresh his memory.

The present little volume, which is No. 82 of the collection Armand Colin, is admirably adapted to such purposes. With the aim of presenting exclusively modern practice, the author omits matters of only historic interest. In discussing apparatus and method, stress is laid upon the advantages and limitations of each type as well as their limits of error. For every type of measurement

considered, a generous number of methods depending upon different principles are described. Instruments are classified according to type and are illustrated by means of line diagrams; the principles upon which they operate are precisely defined by brief but adequate formulated data. The reader has accordingly in compact form an unusually varied collection of instruments and methods for ready reference, and a fertile source of inspiration in the selection of devices best suited to his needs. LUCIEN E. PICOLET.

FIELD ASTRONOMY FOR ENGINEERS AND SURVEYORS. By David Clark, M.A., B.Sc., University of Dublin. viii–164 pages, 12mo. New York, D. Van Nostrand Company, 1926. Price, $3.50.

Socrates would not have approved this book. He deprecated in no uncertain language the application of astronomy to practical purposes. Its real purpose is the ennobling influence on the mind. Modern methods are not of this nature. Man is now employing all the knowledge of nature that can be acquired to developing procedures for his profit or enjoyment.

The book in hand is, as its title states, a "field" manual, a companion for the engineer and surveyor in their everyday duties. The heavens are not absolutely unchangeable, but in their main features sufficiently so to be available for the determination of time and locality. Only brief description is given of the basic principles upon which such determinations rest. The bulk of the text is devoted properly to instruction in the application of astronomical phenomena to measurements. A remark concerning the contrast between the apparent motions of the celestial sphere and the real motion is interesting: "It will be found convenient to disregard the fact that the diurnal motion of the celestial sphere is only apparent and to assume that it is real and that the earth's rotation is annulled."

The book is printed in clear type on good paper, well illustrated by diagrams and formulas, and in pocket size so that it will be a convenient reference companion for the engineer or surveyor in field work.

HENRY LEFFMANN.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 251, Approximations for Column Effect in Airplane Wing Spars. By Edward P. Warner and Mac Short. 20 pages, illustrations, quarto. Washington, Government Printing Office, 1927. Price, ten cents.

The significance attaching to "column effect" in airplane wing spars has been increasingly realized with the passage of time, but exact computations of the corrections to bending moment curves resulting from the existence of end loads are frequently omitted because of the additional labor involved in an analysis by rigorously correct methods. The present report, submitted for publication to the National Advisory Committee for Aeronautics, represents an attempt to provide for approximate column effect corrections that can be graphically or otherwise expressed so as to be applied with a minimum of labor. Curves are plotted giving approximate values of the correction factors for single and two-bay trusses of varying proportions and with various relationships

between axial and lateral loads. It is further shown from an analysis of those curves that rough but useful approximations can be obtained from Perry's formula for corrected bending moment, with the assumed distance between points of inflection arbitrarily modified in accordance with rules given in the report.

The discussion of general rules of variation of bending stress with axial load is accompanied by a study of the best distribution of the points of support along a spar for various conditions of loading.

Report No. 252, The Direct Measurement of Engine Power on an Airplane in Flight with a Hub Type Dynamometer. By W. D. Gove and M. W. Green. 11 pages, illustrations, quarto. Washington, Government Printing Office, 1927. Price, ten cents.

This report describes tests made at the Langley Memorial Aeronautical Laboratory of the Committee to obtain direct measurements of engine power in flight. Tests were made with a Bendemann hub dynamometer installed on a modified DH-4 airplane, Liberty 12 engine, to determine the suitability of this apparatus.

This dynamometer unit, which was designed specially for use with a Liberty 12 engine, is a special propeller hub in which is incorporated a system of pistons and cylinders interposed between the propeller and the engine crank shaft. The torque and thrust forces are balanced by fluid pressures, which are recorded by instruments in the cockpit.

These tests have shown the suitability of this type of hub dynamometer for measurement of power in flight and for the determination of the torque and power coefficients of the propeller.

Report 254, Distribution of Pressure over Model of the Upper Wing and Aileron of a Fokker D-VII Airplane. By A. J. Fairbanks. 14 pages, illustrations, quarto. Washington, Government Printing Office, 1927. Price, ten cents.

This report describes tests made in the atmospheric wind-tunnel of the Committee for the purpose of determining the distribution of pressure over a model of the tapered portion of the upper wing and the aileron of a Fokker D-VII airplane. Normal pressures were measured simultaneously at 74 points distributed over the wing and aileron. Tests were made throughout the useful range of angles of attack with aileron setting ranging from $-20°$ to $+20°$. The results are presented graphically.

It was found that the pressure distribution along the chord is in general similar to that of thick tapered airfoils previously tested. The maximum resultant pressure recorded was five times the dynamic pressure. The distribution of the air load along the span may be assumed to be uniform for purposes of design.

Aileron displacements affect the pressures forward to the leading edge of the wing and may increase the air load on the outer portion of the wing by a considerable amount. With the wing at large angles of attack, the overhanging portion of the aileron creates usually a burbled flow and therefore a large drag. The balance reduces the control stick forces at small angles of attack

for all aileron displacements. At large angles of attack it does this for small displacements only. With the airplane at its maximum speed, an angle of attack of 18° and a down aileron displacement of 20° the bending moment tending to break off the overhanging portion of the aileron will be greater than that caused by a uniform static load of 35 pounds per square foot.

THE DEVELOPMENT AND PRESENT POSITION OF CHEMICAL ANALYSIS BY EMISSION SPECTRA. By F. Tyman, F.R.S. 43 pages, illustrated, 8vo. London, Adam Hilger, Ltd. Price, 2s. 8d. net.

The two lectures in this book are based on a single lecture delivered before the Sheffield Metallurgical Association. The book is partly, of course, a statement of the forms of apparatus manufactured by the publisher, who has acquired a prominent position in the whole field of practical application of spectral phenomena. The application of spectrum analysis to metallurgical work has had periods of activity and repose. A widespread interest in the general subject was developed in about the sixth decade of the last century by the discovery of cesium and rubidium by Bunsen and Kirchhoff. The book covers the latest developments of the application of luminous radiations to qualitative analysis.

THE POLARIMETER. By Vivian T. Saunders, M.A. 31 pages, illustrated, 8vo. London, Adam Hilger, Ltd. Price, 1s. 6d. net.

This is a reprint of a lecture on the theory and practice of polarimetry. It includes a brief but interesting and valuable summary of the history of the development of the instrument and an account of its more important practical applications. The lecture was illustrated by lantern slides, the designs of some of which are reproduced in the book. It appears from the historical summary that the phenomenon of double refraction was noted by Bartolinus, a Dane, in 1670. The rotary power of turpentine, the first observation of this kind, was discovered by Biot. One of Biot's papers was published in the first decade of the nineteenth century with his title as "Citizen Biot."

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Bibliography of Aeronautics, 1924. By Paul Brockett. 114 pages, 8vo. Washington, Government Printing Office, 1926. Price, twenty-five cents.

The volume covers the literature published from January 1 to December 31, 1924, and continues the work of the Smithsonian Institution issued as Volume 55 of the Smithsonian Miscellaneous Collections, which covered the material published prior to June 30, 1909, and the work of the National Advisory Committee for Aeronautics as published in the Bibliography of Aeronautics for the years 1909 to 1916, 1917 to 1919, 1920 to 1921, 1922 and 1923.

As in the Smithsonian volume and in the Bibliography of Aeronautics for the years 1909 to 1916, 1917 to 1919, 1920 to 1921, 1922 and 1923, citations of the publications of all nations have been included in the languages in which

these publications originally appeared. The arrangement is in dictionary form with author and subject entry, and one alphabetical arrangement. Detail in the matter of subject reference has been omitted on account of the cost of presentation, but an attempt has been made to give sufficient cross-reference for research in special lines.

PUBLICATIONS RECEIVED.

Towards the Open. A preface to scientific humanism, by Henry Chester Tracy. With an introduction by Julian Huxley. 257 pages, 8vo. New York, E. P. Dutton and Company, 1927. Price, $3.50.

History of the Sciences in Greco-Roman Antiquity, by Arnold Reymond, Professor of Philosophy at the University of Lausanne, translated by Ruth Gheury de Bray. 245 pages, 12mo. New York, E. P. Dutton and Company, no date. Price, $2.50.

Problems of Modern Physics. A course of lectures delivered in the California Institute of Technology, by H. A. Lorentz, professor in the University of Leiden. Edited by H. Bateman. 312 pages, illustrations, 12mo. Boston, Ginn and Company, 1927. Price, $3.60.

The Polarimeter. A lecture on the theory and practice of polarimetry, by Vivian T. Saunders, M.A. 31 pages, illustrations, 8vo. London, Adam Hilger, Ltd., no date. Price, one shilling 7d.

Two Lectures on the Development and Present Position of Chemical Analysis by Emission Spectra, by F. Twyman, F.R.S. 43 pages, illustrations, 8vo. London, Adam Hilger, Ltd., no date. Price, two shillings 8d.

Field Astronomy for Engineers and Surveyors, by David Clark, M.A., B.Sc. 164 pages, illustrations, 12mo. London, Constable and Company, 1926. Price, $3.50.

CURRENT TOPICS.

An Experiment Planned to Test the Ether Theory of Light. A. H. BUCHERER. (*Zeit. f. Phys.*, **41**, No. 1.)—Much interest is being manifested at the present time in the Michelson-Morley experiment. To the negative results obtained from it arose the supposition that the dimension of moving matter is shortened in the direction of motion and, further, they had much to do with the establishment of the Theory of Relativity. On the other hand, Dayton C. Miller within the last years has obtained positive results that are interpretated as militating against the theory. More recently both in America and in Europe other investigations have challenged the accuracy of Miller's results so that at the present time the whole matter is under consideration and much hangs on the issue of the scientific process under way.

There are points in the interpretation of any results furnished by the experiment that are not clear. For example, there is uncertainty as to just what takes place when light is reflected from a mirror in rapid motion. Thus Professor Bucherer is led to seek a crucial experiment free of theoretical complications. He suggests the use of a tube whose length is 10,000 times its diameter, because the velocity of light is about 10,000 the velocity of the earth in its orbit about the sun. Let the tube be placed in the direction of the earth's motion and let a beam of parallel light enter at one end. It will reach the other end. On the other hand, turn the tube so that its length is at right angles to the direction of the earth's motion and again send in at the end a beam travelling parallel to the tube. As the light advances along the tube the latter is carried sidewise by the earth so that finally the light will strike the side of the tube instead of emerging at the end. This result is predicted on the basis that light from a moving source spreads out in the ether just as it would from a source at rest.

Actual experiments according to the method mentioned are in preparation. Instead of the eye a thermo-element or eventually a photographic plate will be used to register the arrival of light at the end of the tube. "However this experiment may turn out, whether for or against the theory of ether previously held, the problem of the physicist remains to form a picture of optical processes that will explain the phenomena of polarization and of diffraction by means of the properties of an elastic medium." G. F. S.

The Continuous Spectrum of Hydrogen. O. OLDENBERG. (*Zeit. f. Phys.*, **41**, No. 1.)—There was a time when it was said that continuous spectra could be obtained only from solids and liquids. Now we know better, for hydrogen possesses two such spectra. One, discovered in the light of stars by Hartmann and interpreted on

Bohr's theory by Debye, connects with the end of the Balmer series. The other found by E. P. Lewis and the subject of several explanations, extends from the Schumann region of the spectrum up well into the visible part. It is the second continuous spectrum with its range from 1450 to 5500 Ångström units that is the subject of this paper.

That it really is due to hydrogen was first established. It had been claimed that this spectrum cannot be got from hydrogen at low pressure and carefully dried and that water vapor, not hydrogen, is the origin. Experiments were conducted with very carefully dried hydrogen. At low pressure the continuous spectrum was relatively less intense but it was certainly present. At high pressures it was very bright and extended up to 5500 Å. U. When a tube was giving the continuous spectrum the admission of argon extinguished it.

It was of interest to examine whether all parts of the continuous spectrum of hydrogen reacted in the same way to modifying influences. A difference in effect might well exist, especially in consideration of the occurrence of a maximum of intensity at 4000 Å. U. in the long spectrum. By means of a quartz prism spectroscope photographs were taken that covered a range from 2200 to 5500 Å. U. at one exposure. Increasing the pressure of the hydrogen, adding to or subtracting from the quantity of argon present, changing the density of current in the ratio 1:80, the application of a magnetic field of 20,000 gauss, all of these failed to divide the spectrum into portions differently affected. "To every change in the discharge tube the continuous spectrum reacts as a uniform whole. It therefore probably is due to a single elementary process."

G. F. S.

Another Centenary.—Many of the inventions which we are using to-day have become so much a part of our life that we can scarcely imagine a condition of society without them. Presumably the telephone and automobile will occur to most persons as being the promptings of this remark, but it has a humbler source. The ordinary match, the source of much convenience, but unfortunately also of much damage, has now a history of a little over one hundred years. From an article in *Nature* (1927, **119**, 495) we learn that it was on April 7, 1827, that John Walker, a pharmacist of Stockton-on-Tees, recorded in his sales book the first sale of his newly invented "Friction Lights." Scarcely anybody is now living who recollects the old flint and tinder days, but some of us have heard in earlier years the stories of our ancestors as to the extreme annoyance and delay in getting a light in that manner. A distinguished professor of one of our medical schools said in his latter years that he had seen many of the inventions of the nineteenth century come into vogue, but the friction match was to him the most acceptable. Further back, of course, we have the matchlock used by the soldiers, long ropes of

combustible material kept burning in order to be ready to ignite the powder. It was with this kind of a weapon that the Puritan and the Parliamentary armies fought in the Cromwellian days and we need not be surprised that the pious leader of the Puritan army gave the advice to his troops "Trust in the Lord and keep your powder dry."

John Walker's match, of which a few specimens have fallen into the hands of Prof. William A. Bone, F.R.S., on an examination proves to be tipped with a mixture of potassium chlorate and antimonous sulphide made into a paste with gum and starch. In 1829 a notice appeared in the *Quarterly Journal of Science, Literature and Art*, under the title of "Instantaneous Light Apparatus," in which it is stated that Mr. Walker "supplies the purchaser with prepared matches, which are put up in tin boxes, but are not liable to change in the atmosphere, and also with a piece of fine glass-paper folded in two. Even a strong blow will not inflame the matches, because of the softness of the wood underneath, nor does rubbing upon wood or any common substance produce any effect except that of spoiling the match; but when one is pinched between the folds of the glass-paper, and suddenly drawn out, it is instantly inflamed."

Other claimants of course have appeared and very unfortunately in the Report of Juries of the Exhibition of 1851, Warren de la Rue and A. W. Hofmann stated that friction matches appeared about 1832 without even mentioning Walker's invention. The matches to which they alluded were known as "Congreves" and were introduced into England from Germany and Austria, but were the invention of a French chemist, Charles Sauria. In 1913 *Punch* published a few verses in the honor of Walker, but otherwise he has not received much glory from his fellow countrymen.

Considerable modification has of course been made in the nature of the match. Many persons still remember the old blue-tipped match with its sulphur coating and the excessively irritating character of the gas thus produced. The modern match is free from this objection.

H. L.

Cosmic Aspects of Atmospheric Electricity. L. A. BAUER. (*Science*, April 1, 1927.)—Since there is no accepted theory of the cause and maintenance of the negative electrical charge of the earth, it is desirable to observe and measure the electrical field in the atmosphere and to detect and follow its changes through the day and the year. In this paper are discussed the data only for "days of no negative potential and no pronounced disturbances."

A marked difference between terrestrial magnetism and atmospheric electricity lies in this, viz., "the fluctuations of the atmospheric-electric elements are of the same order of magnitude as the absolute elements themselves—not fractions of a per cent. as is usually the case with the fluctuations of the magnetic elements." From results obtained on the cruises of the non-magnetic *Carnegie*, Mauchly was led to the conclusion that a wave, recurring every twenty-four hours

and appearing simultaneously all over the earth, is the chief constituent in the daily variations in the potential gradient over a large portion of the earth. Observations over land areas confirmed his deductions. "It certainly must be regarded as an impressive and significant fact that the potential gradient of atmospheric electricity passes nearly everywhere through extreme values during twenty-four hours at about the same universal times, irrespective of whether the observing station be enveloped by sunshine or by darkness."

A study of the potential gradient in the atmosphere shows that its greatest values for both northern and southern hemispheres occur from October to March, when the earth is nearest to the sun and are least from April to September when the distance between the two bodies is greatest. The daily range of the gradient is found to vary throughout the year in just about the same manner as the amount of the gradient itself. Doctor Bauer further claims that there is some connection between the number of sun-spots and the value of the potential gradient and of the daily and yearly ranges of this quantity. It is too soon to investigate secular changes in the gradient. G. F. S.

Demonstration of the Behavior of Bodies with Non-conducting Surfaces in Electrostatic Fields. L. G. VEDY. (*Proc. Physical Soc.*, London, **39**, Pt. 2.)—The actions here considered were noted a year or two ago by S. W. Richardson. It seems that they were described as early as 1921 in V. E. Johnson's "Modern High Influence Machines."

Any body, free to rotate and consisting of a dielectric or covered with such material, starts to rotate when placed between the poles of a Wimshurst machine. This was demonstrated by suspending on threads bits of paraffin or sealing wax and a glass beaker between the knobs of a machine. Better results were attained by mounting the experimental bodies on bearings such as needles in glass sockets. Brass balls covered with paraffin rotated, the thicker the layer the faster being the rotation. Covering the insulator with conducting foil caused the rotation to disappear. Also a partial conductor, such as cork, was set in rotation. Without the brush discharge the effect is not found. The rotating body generally becomes charged with electricity of the same kind as that on the knob contributing the greater discharge. If the test body be hung within a glass beaker or between two plates of ebonite, no rotation occurs. G. F. S.

Measurement of the Velocity of Light between Mount Wilson and Mount San Antonio. A. A. MICHELSON. **Measurement of Length of Line Used in Determination of Velocity of Light.** WILLIAM BOWIE. (*Astrophys. J.*, Jan., 1927.)—In a preliminary report on his measurements of the velocity of light made on Mount Wilson the velocity in air was found to be 299,735 km. per sec. and the velocity in vacuum 67 more, or 299,802 km. per sec. Essen-

tially the method is this. A beam of light is reflected on Mount Wilson from one of the surfaces of an octagonal mirror rotating about a vertical axis. It travels more than 35 km. to Mount San Antonio, where it is reflected back to Mount Wilson. Here it falls on the next face of the octagonal mirror, the speed of rotation being maintained constant at the proper value to make this possible, in this case 528 revolutions per second. Thus in one-eighth of 1/528 sec. the light travels twice the distance 35,425.5 m. or with a velocity of 299,266 km. per sec. This is subject to certain corrections.

With an octagonal mirror of glass in a series of ten preliminary determinations the lowest velocity in air was 299,651 and the highest 299,725 km. per sec., with the mean 299,689. The definitive measurements were begun in June, 1926, and continued to September, 1926. A group of twelve measurements, made with the same glass octagon, gave as a mean for the velocity in air 299,746 km. per sec. Mean value with a glass twelve-facet mirror, 299,729; with a glass sixteen-facet mirror, 299,736; a second series with the same mirror, 299,722; with a steel twelve-facet mirror, 299,729; with a steel octagon, 299,728. The agreement of results is striking when all the series taken with the same mirror are used in getting the mean value for that mirror:

Glass,	8 sides.....	299,797	km./sec. in vacuum
Steel,	8 sides.....	299,795	
Glass,	12 sides.....	299,796	
Steel,	12 sides.....	299,796	
Glass,	16 sides.....	299,796	

The final value given is 299,796 km. per sec. *in vacuo*. The rate of rotation of the mirrors was measured with extreme accuracy. The motive power was an air-blast coming through two nozzles and striking on the vanes of a paddle wheel. It was possible to keep the speed of rotation constant for several seconds as judged by a stroboscopic method.

Encouraged by "the ready success of the measurements at a distance of twenty-two miles, the majority of which were made under conditions not the most favorable (haze and smoke from forest fires; imperfections of surfaces of the revolving mirrors)." Professor Michelson made a trial with a mirror on Mount San Jacinto, eighty-two miles away, but the light was so weakened by smoke that measurements were impossible. In the hope that winter rains will improve the visibility he states that a further attempt was to be made last December to extend the range of the experiment. Of course the final results are no more accurate than the measurement of the distances is, of which the distance from one mountain to the other is the longest by far. This was measured by the Coast and Geodetic Survey with every refinement. The actual error is certainly less than 1 part in 300,000. "It is believed that the length of this line has been deter-

mined with greater accuracy than that of any other line of triangulation in this or any other country." The probable error from field measurements and observation alone is 1 part in 6,800,000.

G. F. S.

On the Proportionality of Mass and Weight. H. H. POTTER. (*Proc. Roy. Soc.*, A 765.)—The nuclei of all elements are probably composed of hydrogen and helium nuclei. The nuclei of those substances on which gravitational experiments have been made are probably formed of helium nuclei. In order to see whether the composition of the nuclei makes any difference, experiments were made three years ago to compare the gravitational acceleration of ammonium fluoride and paraffin with that of brass. It was calculated that these two substances have 24 and 15 per cent. of hydrogen respectively, while brass consists almost altogether of helium. The experiment appeared to show that the substances rich in hydrogen had an acceleration greater by 1 part in 70,000 than that of brass. This comparison has recently been repeated with the use of an Eötvos torsion balance. The outcome is that "no difference in the mass-weight ratios of the three substances could be observed, so that it would appear that the mass-weight ratios of helium and hydrogen do not differ by more than one part in 3×10^6."

G. F. S.

THE FRANKLIN INSTITUTE

OFFICERS FOR 1927

President	WM. C. L. EGLIN
Vice-presidents	HENRY HOWSON C. C. TUTWILER WALTON FORSTALL
Secretary	HOWARD McCLENAHAN
Assistant Secretary and Librarian	ALFRED RIGLING
Treasurer	BENJAMIN FRANKLIN
Controller	WILLIAM P. JACKSON, JR.

Board of Managers

JAMES BARNES
GEORGE H. BENZON, JR.
CHARLES E. BONINE
EDWARD G. BUDD
FRANCIS T. CHAMBERS
G. H. CLAMER
THEOBALD F. CLARK
WALTON CLARK
CHARLES DAY
ARTHUR W. GOODSPEED
CLARENCE A. HALL
ALFRED C. HARRISON
NATHAN HAYWARD
GEORGE A. HOADLEY
ROBERT W. LESLEY
MARSHALL S. MORGAN
CHARLES PENROSE
JAMES S. ROGERS
GEORGE D. ROSENGARTEN
E. H. SANBORN
HASELTINE SMITH
SAMUEL T. WAGNER
J. T. WALLIS
WILLIAM C. WETHERILL

PRESS OF
J. B. LIPPINCOTT COMPANY
PHILADELPHIA